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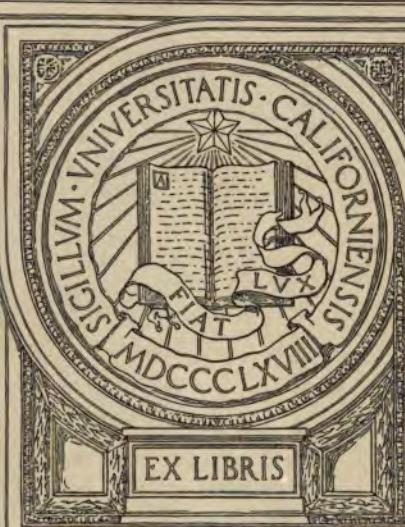
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**A COURSE IN  
QUALITATIVE CHEMICAL ANALYSIS**



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# A COURSE IN QUALITATIVE CHEMICAL ANALYSIS

UNIVERSITY OF  
CALIFORNIA

BY

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## PREFACE TO THE SECOND EDITION

THE reception of this book by teachers of Qualitative Analysis, calling for a number of reprintings of the first edition, has been a source of gratification to the Authors. In the revision, some changes and additions, as indicated by the use of the book, have been made. The original plan of the book, however, has been maintained. Some valuable suggestions from others have been utilized. The theory of Electrolytic Dissociation and the Law of Mass Action have been outlined. New methods, some proposed elsewhere and some developed by original work in our qualitative laboratories, have been incorporated. All of the new methods given have been thoroughly tried out.

THE AUTHORS.

NEW YORK CITY,  
July, 1916.



## PREFACE TO THE FIRST EDITION

EXPERIENCE has shown the authors that a quantitative discrimination in Qualitative Analysis for students is rarely exercised, although it is generally conceded that qualitative analysis should serve not only as a means for determining the components in an "unknown," but also, though roughly, the proportions in which the ingredients are present. This failure to gain experience in the evaluation of tests is, we believe, largely due to the fact that in the preliminary work which precedes the analysis of "unknowns," adequate provision is not made whereby the quantitative aspect as well as the qualitative meaning of the results can be simultaneously studied.

In our work the quantitative feature is emphasized, first, by early acquainting the student with the fact that there is a *limit* in the quantity of an element in a definite volume that may be detected by a given reaction; second, by the use of known solutions which are prepared to contain definite amounts of the elements of a group in a definite volume. For example, the label on the bottle states the metallic concentration of its contents, and the student by using a specified volume knows precisely how many milligrams of each metal he is using. The advantages in the use of such a solution are: first, the size of the precipitates may be controlled by the instructor and precipitates of unwieldy bulk avoided; second, and this is the chief advantage, in addition to familiarizing himself with the reactions and separations, the student also learns *the relation between the quantity of metal present and the size of the precipitate which it yields*. The quantitative information thus acquired in the analysis of known solutions is subsequently applied to the

analysis of unknowns. In consequence of this training, the student is able to report not only the qualitative composition of his unknowns, but also approximately their quantitative composition. The value of such training cannot be overestimated. Our students rarely find any difficulty in differentiating between a trace and a significant amount. In the schemes of analysis for the metals, preference has been given in a vast majority of cases to precipitation tests, because of their quantitative significance.

Detailed methods for the preparation of solutions of definite strength are given for the assistance of the instructor.

The value of introducing preliminary experiments in a course in Qualitative Analysis is a mooted question. We believe that they should be restricted to those which are utilized in the schemes of separation. Experience has shown us that it is a good plan to have in the laboratory several sets of bottles containing solutions of known strength of the salts of the various metals. The students are encouraged to use these to verify any of the preliminary tests in case of doubt. By comparing in special cases the results obtained with known solutions with those obtained with the unknown, a definite knowledge of that particular reaction is fixed in the student's mind. Students should be encouraged to use short cuts, and the use of the preliminary test as a means of indicating short cuts.

It is assumed that the student who begins the study of Qualitative Analysis has had a course in laboratory work in General Chemistry, and has thus become familiar with such operations as making solutions, precipitations, evaporation, ignitions, and the preparation of borax beads. He has also become familiar with the term "solubility." For these reasons such matters have received but scant attention in this book.

The student should have had not a little experience in writing equations. The application of his knowledge, often meager, to the processes of oxidation and reduction, as well as to the mode of operation of reagents producing these changes, is not always clear; or his knowledge is not sufficient to cope with the cases met with in Qualitative Analysis. For this reason

these matters have been brought together and coördinated with some detail in the beginning of the book.

The essential features of this book may be seen from the plan which is here briefly outlined.

1. The *chief reactions* of the metals are first given with sufficient detail and completeness to enable the student to thoroughly understand the basis of and the *limitations* to the schemes of analysis adopted. Reactions not utilized in the schemes are also given to supply information which may be turned to account in making additional confirmatory tests and in devising schemes other than those given; they also supply a number of qualitative facts upon which important quantitative methods are based. As the vast majority of students who take Qualitative Analysis subsequently pursue a course in Quantitative Analysis, this information supplies the foundation of fact which we believe should be given in the qualitative course.

2. An *outline of the method of analysis* to be employed follows. This is in the nature of a résumé of the chief reactions, in which distinctions are emphasized with a view to their use in separations. Details in manipulation are purposely omitted in this discussion, in order that the main features and chemistry thereof may be clearly understood.

3. The *scheme of analysis* is then taken up. The directions are clear, especial attention being given to the amounts of reagents to be taken, as well as the most appropriate vessel to be used and its size.

4. Then follow *notes*. Under this head, additional information, which would obstruct the reading of the text, is supplied. This information is intended to supply the reasons for unusual details or procedures in the text and precautions that are to be taken, but it applies chiefly to matters relating to the correcting of errors and to the clearing up of doubtful results. Supplying the reasons for every step, it is believed, will go a long way toward doing away with the too frequent practice of blindly following directions.

The so-called rarer elements have been omitted, and some of the commoner ones also, as their study is not essential in a

first course in Qualitative Analysis. This is essentially a practical book and not the place to exploit any particular hypothesis or theory. Its contents are directed toward the study of reactions and the operations and methods made use of in the identification of unknown substances or mixtures. Discussions of the theory of electrolytic dissociation and the mass action law are now presented in courses in General Chemistry. These may be further applied in lectures, which form an integral part of the study of Qualitative Analysis, and are of especial value when accompanied by collateral reading of special works on the theoretical phases of the subject.

The authors are aware that no directions, however detailed and carefully written, can replace the resourcefulness of the instructor; he should be particularly observant during the first laboratory periods when methods of work are about to be acquired, and should be quick to give personal attention to those who need it most. There are those to whom skill in manipulation comes naturally, but it should be remembered that those not so gifted may, by perseverance and constant practice, acquire an unusual degree of skill. A bright student will soon learn that he may carry on two or more operations at once, as filtration of one liquid while evaporating another, without the suggestion of an automatic teacher; but the work of the class as a whole will suffer unless the instructor is alive and richly suggestive.

In the recitations, questions may be asked concerning separations and tests, other than those given in the schemes, but which are given in the descriptive portion of the book; these serve to stimulate original thinking and give opportunity for the exercise of individual ingenuity. Written quizzes have little value beyond securing figures for grading, unless the papers, after being corrected, are discussed with the students.

Well-known works on the subject have been drawn from more or less. We wish especially to mention Fresenius, Prescott and Johnson, Treadwell, Knoevenagel, and A. A. Noyes. Conflicting statements appear in many books; in some cases

consultation of the original sources sufficed, in others research was necessary, to arrive at a decision.

We are indebted to Mr. W. A. Hamor, who assisted in following the proof sheets.

**CHARLES BASKERVILLE.  
LOUIS J. CURTMAN.**

**COLLEGE OF THE CITY OF NEW YORK,  
November, 1910.**



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## INTRODUCTION

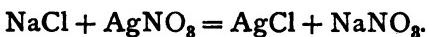
THAT branch of chemistry concerned with the problem of determining the composition of substances or mixtures of substances and identifying them is called **Analytical Chemistry**. Substances are identified by their properties which, for any given substance, are unchangeable and fixed. The problem of identifying a substance, therefore, resolves itself into a determination of a sufficient number of the properties of the substance in question. For a mixture of substances it is frequently necessary to separate the components before the latter can be identified.

The term *analysis* is used in Analytical Chemistry to denote the systematic examination of a substance, and includes all the operations, whether analytic or synthetic, involved in the process of identifying a substance. An analysis may be either *qualitative* or *quantitative*. If we satisfy ourselves that a ten-cent piece consists of copper and silver, our knowledge is *qualitative*; but if we ascertain how much copper and silver are contained in a given weight of this alloy, our knowledge becomes *quantitative*. For qualitative purposes, only a few of the many properties possessed by a substance are utilized for its identification. In general, those which are striking and most rapidly determined are the ones selected; chief among these are color, state of aggregation, solubility, and certain chemical properties.

### TERMS EMPLOYED IN QUALITATIVE ANALYSIS

If to an aqueous solution of sodium chloride we add a water solution of silver nitrate, a white, curdy, solid substance forms and settles to the bottom of the containing vessel. The chemical change, as evidenced by the formation of the new substance,  $\text{AgCl}$ , and brought about by mixing these solutions, is called a **reaction**. The  $\text{AgNO}_3$  solution employed to produce this reaction is called the **reagent**. The solid, insoluble  $\text{AgCl}$  is

called the **precipitate**. Any reaction which is accompanied by the formation of a precipitate is called a precipitation reaction and the process of forming a precipitate is known as **precipitation**. If we allow the precipitate to settle and carefully pour off the clear supernatant liquid, the process is known as **decantation**. If, without allowing the precipitate to settle, we pour the liquid holding the precipitate in suspension on a filter paper, supported in a funnel, or other design of filtering apparatus, the liquid will pass through the fine pores of the filter and will be thus separated from the precipitate, which will remain on the paper. This process is known as **filtration** and is frequently resorted to for the separation of a liquid from a solid. The precipitate on the filter is sometimes called the **residue**, while the liquid which passes through is called the **filtrate**. The equation for the reaction, omitting consideration of the water, is—



Assuming that an excess of silver nitrate has been used, the precipitated and filtered AgCl will be wet with a solution containing NaNO<sub>3</sub> and AgNO<sub>3</sub>. As these are soluble in water, it is evident that they may be removed by treating the precipitate on the filter with water. The process of removing soluble impurities from insoluble substances by treatment with water is known as **washing**.\* All precipitates should be thoroughly washed. Much time will be saved in washing precipitates by allowing each portion of water completely to pass through the filter before adding the next. The completeness of the washing is ascertained by testing a portion of the last washings for the substance it is desired to remove. In the above case, after washing several times with small amounts of water, the last portion should be tested by adding to it a little NaCl solution. If no precipitate is formed, the washing may be considered complete; if a precipitate or cloudiness is obtained, it is an indication that all the AgNO<sub>3</sub> has not been washed out of the precipitate. In the latter case, the washing should be continued until a negative test with NaCl is obtained.

\* Water is used here as the typical solvent.

**GENERAL DIRECTIONS FOR LABORATORY WORK**

Order and cleanliness are essential to success in qualitative analysis. It is a good plan never to put away apparatus until the latter is clean and ready for use. Beakers, evaporating dishes, and funnels, after being thoroughly washed, should finally be rinsed with distilled water, inverted, and allowed to drain and dry on a clean towel which has been spread out on the floor of the cupboard of the desk. Every piece of apparatus in the desk should have a fixed place. Iron ware should not be kept in the same drawer or compartment with glass ware. Some attention should also be given to the arrangement of apparatus on the desk. In general, the desk space should be roughly divided into two parts—namely, one reserved for heating, and the other for filtering, washing, testing, etc. Reagent bottles must never be allowed to accumulate on the desk, but should be returned to their proper places immediately after use. Accidents, which occasionally happen even to the most careful workers, must receive immediate attention; the broken glass should be collected and thrown into a special crock provided for this purpose; and the desk top should be sponged off, the apparatus cleaned, and the analysis begun anew. Vessels containing solutions or precipitates which are to be set aside for future examination should be properly labeled.

**Reagents.** The bottles on the desk are filled with solutions known as **reagents**. They should occasionally be wiped off with a moist rag and every effort should be made to keep their contents pure. When once an impurity is allowed to enter a reagent bottle, the reagent becomes worthless. The importance of the care of reagents will be appreciated when it is remembered that the value of the whole analysis is dependent upon their purity. The bottles should always be kept properly stoppered, and the stopper under no circumstances should be placed on the desk, where it is likely to take up impurities and thus eventually contaminate the reagent. The student should make it a rule always to hold the stopper between the fingers while using the bottle and to return it immediately after use;

in this way danger of contamination from the desk is avoided. Acids of two strengths will be found on the desk. Before using the reagents, the student should be sure that he is using the proper ones. If he will learn in each case the reason for adding the reagent, the error arising from the use of the wrong reagent will seldom, if ever, occur. Too much reagent is worse than adding too little. Reagents should always be added drop by drop and should never be used in great excess, unless otherwise directed; but under no circumstance is an excess of reagent to be poured back into the bottle.

All operations which result in the production of fumes of any kind must be conducted under the hood, with the window of the latter almost completely closed.

#### THE THEORY OF ELECTROLYTIC DISSOCIATION \*

When a substance such as sugar is added to water and the latter stirred, there results a homogeneous mixture known as a *solution*. The dissolved substance, the sugar, is called the *solute*; the water in which the sugar dissolves, the *solvent*. In a similar manner we may prepare an aqueous solution of salt. An experimental study of the properties of aqueous solutions discloses the fact that some conduct the electric current, while others do not; *e.g.*, a solution of sugar does not permit the passage of the current, while on the other hand a solution of salt is found to be a good conductor of electricity. It is natural to suppose that the solute which is different in the two cases cited is responsible for the difference in behavior. Experiment confirms this supposition. We may therefore divide substances soluble in water into two classes, viz. (*a*) those which conduct the electric current and (*b*) those which do not. The former are called *electrolytes*, the latter *non-electrolytes*. Acids, bases, and salts are electrolytes. Sugar, glycerol, urea, ethyl alcohol, are non-electrolytes.

\* The theoretical matter dealt with in this section is generally considered more or less in preliminary courses in General Chemistry. A brief summary is here given partly to refresh the student's knowledge, but chiefly to emphasize certain principles which have many applications in the field of qualitative analysis.

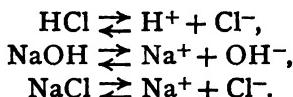
A study of the freezing and boiling points of aqueous solutions leads to a similar classification. Thus if 60 grams (the molecular weight) of urea are dissolved in 1000 grams of water, the resulting solution, which is said to contain one mole of urea, is found to freeze at  $-1.86^{\circ}$  C. The same result is obtained when a solution containing one mole of any other non-electrolyte is cooled to its freezing point. In general, it has been found that the freezing point of a dilute solution of a non-electrolyte is solely dependent upon the *number* of moles in solution, provided that in freezing only the pure solvent separates out. Thus the freezing point of a solution of 50 grams of methyl alcohol in 1000 grams of water is found to be  $-2.90^{\circ}$ . This is what we should expect, since the number of moles in solution is  $\frac{50}{46}$ , or 1.56. And as the freezing point is lowered  $1.86^{\circ}$  for each mole of a non-electrolyte, the total lowering should be  $1.86 \times 1.56 = 2.90$ .

On the other hand, if we dissolve  $\frac{1}{10}$  of a mole (5.85 grams) of sodium chloride in 1000 grams of water and determine its freezing point, we should find it to be  $-0.350^{\circ}$ . If sodium chloride were a non-electrolyte, the freezing point should be  $-0.186$ . On comparing these results we see that the lowering is  $\frac{.350}{.186}$ , or 1.88, times greater than that which we should obtain if salt were a non-electrolyte. A comparative study of the boiling points of molar solutions of electrolytes and non-electrolytes reveals a similar difference, viz. that solutions of electrolytes boil at a higher temperature than solutions of non-electrolytes of the same molar concentration. On the basis of an experimental study of three of the properties of solutions, viz. conductivity, boiling point, and freezing point, we are thus led to a division of soluble substances into two classes, electrolytes and non-electrolytes.

Moreover, a study of the reactions of electrolytes in solution shows that they behave in solution as though their constituent parts were independent of each other; thus solutions of KCl, NaCl, BaCl<sub>2</sub>, and FeCl<sub>3</sub> each give the same precipitate with a solution of AgNO<sub>3</sub>, Ag<sub>2</sub>SO<sub>4</sub>, AgC<sub>2</sub>H<sub>8</sub>O<sub>2</sub>, or AgF. In other

words, the chlorine in the first series of salts reacts independently of the metal with which it is united to give a precipitate of  $\text{AgCl}$  when any soluble salt of silver is added, the silver acting independently of the acid radical with which it is united in the dry state. In general, all electrolytes having a common component will respond to a reaction that is characteristic of that component.

All these differences in the properties of solutions of electrolytes and non-electrolytes find their explanation in the Theory of Electrolytic Dissociation which was proposed by Svante Arrhenius in 1887. According to this theory when an electrolyte is dissolved in water, it breaks up or dissociates more or less completely into electrically charged particles called *ions*. These ions are of two kinds, viz. those carrying positive electricity called *cations* and those bearing negative charges called *anions*. As the resulting solution is electrically neutral, the sum of all the positive charges in solution must be equal to the total number of negative charges. The change which takes place according to this theory when an electrolyte is dissolved in water may be formulated as follows :—

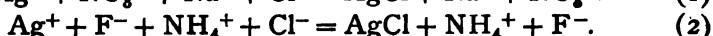


The above shows that dissociation is to be looked upon as a reversible reaction. The extent of the dissociation varies with the dilution ; and at infinite dilution, the dissociation may be regarded as complete. The + sign between the ions indicates that they are to be regarded as independent particles with specific chemical and physical properties. The possession of a charge of positive electricity renders the sodium ion ( $\text{Na}^+$ ) totally different from the elementary substance sodium. The same holds true for the hydrogen ion, which is distinctly different from the electrically neutral hydrogen gas. Metallic sodium, as is well known, reacts violently with water; sodium ions do not. We usually recognize hydrogen ions by their sour taste and by their property of changing the color of solutions of certain sub-

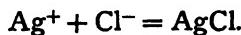
stances, called indicators. Hydrogen gas does not exhibit these properties.

By passing a current through an aqueous solution of NaCl, the electro-negative chlorine ions will travel towards the positive electrode, give up their charges to the latter, and become electrically neutral chlorine, which exhibits the well-known properties of this element. The electro-positive sodium ions will at the same time migrate to the positive electrode. Sodium ions are not discharged at this pole owing to the fact that the hydrogen ions, formed by the dissociation of the water, lose their charges more readily than do the sodium ions. Consequently on passage of the current, the hydrogen ions lose their charge and electrically neutral hydrogen escapes at the positive electrode.

Before taking up the applications of the ionic theory let us see how it accounts for the facts mentioned in the early part of this discussion. Since the depression of the freezing point is dependent upon the number of particles of the dissolved substance in a given weight of the solvent, it follows that a solution of an electrolyte should depress the freezing point more than a solution of non-electrolyte of the same molar concentration, for the reason that in the former we should have a greater number of particles, each molecule of the electrolyte being capable of yielding at least two ions. The same explanation applies to the observed differences in the boiling points. The existence of electrically charged ions in solutions accounts for the conductivity of solutions of electrolytes; and the failure of solutions of non-electrolytes to conduct the current is due to the absence of ions. Finally, we have to consider how the ionic theory accounts for the independent behavior of the components of electrolytes in solution, which, as already mentioned, makes it possible for salts having a common component to respond to a common reaction. Since all chlorides yield chlorine ions, it is perfectly clear why they should all give a precipitate with any soluble silver salt, for the latter, according to the ionic theory, supplies silver ions. This can be best seen by writing the equations for the reaction in ionic form:—



If we cancel in each equation the ions which appear on opposite sides, equations (1) and (2) become :—



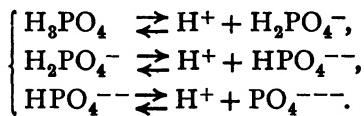
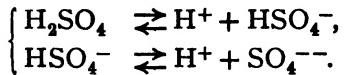
The last equation states that when silver and chlorine ions are brought together, silver chloride is formed; and as the latter is a difficultly soluble substance, a precipitate of  $\text{AgCl}$  is generally obtained. Hence we say that Ag ions are a test for Cl ions, and *vice versa*. From solutions,  $\text{AgCl}$  is formed only by the combination of Ag and Cl ions; therefore solutions of  $\text{KClO}_3$  or  $\text{CHCl}_3$  do not yield a precipitate with silver nitrate for the reason that no chlorine ions are formed by either of these substances in solution. Chloroform in aqueous solution does not conduct the electric current, giving no evidence of dissociation, and hence yields no chlorine ions. Potassium chlorate does ionize in solution, but the ions are  $\text{K}^+$  and  $\text{ClO}_3^-$ .

**Acids and Bases.** In terms of the ionic theory an acid may be defined as a substance which, when dissolved in water, dissociates with the formation of hydrogen ions.

Thus



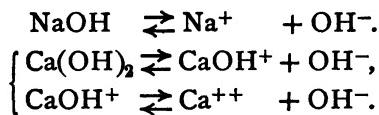
Dibasic acids dissociate in two and tribasic acids in three stages, as shown below :—



Thus a solution of sulphuric acid may contain, besides the undissociated acid, the ions H and  $\text{HSO}_4^-$ . All the characteristic properties of acids in solution — viz. (1) sour taste, (2) the ability to change the colors of indicators, (3) the ability to give

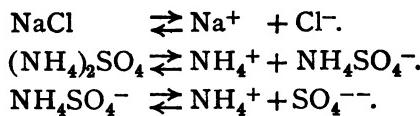
off hydrogen gas when treated with certain metals, (4) the power to neutralize bases — are due to the presence of hydrogen ions. The hydrogen ions are thus the active constituents of acid solutions. The differences in the strengths of acids are due to variations in the extent to which they are dissociated. We thus distinguish two classes of acids. Those which dissociate largely and thus supply a high concentration of hydrogen ions, and those which dissociate slightly and thus yield a low concentration of hydrogen ions; the former are called strong, the latter weak, acids.

The active component of solutions of bases is the hydroxyl ion ( $\text{OH}^-$ ), and to it are attributable all the characteristic properties of bases, viz., (1) the ability to turn red litmus blue, (2) the alkaline taste, (3) the power to neutralize acids. We may define a base, therefore, as a substance which, when dissolved in water, dissociates with the formation of  $\text{OH}$  ions. The following are examples :—



Di-acid bases dissociate in two steps as shown above. As in the case of acids, we distinguish two classes of bases, depending upon the degree to which they are dissociated. A strong base yields a large percentage of  $\text{OH}$  ions; a weak base dissociates feebly, yielding a small concentration of  $\text{OH}$  ions.

Salts yield on dissociation negative ions of the acid and positive ions of the base, as shown here :—



**Conductivity and Dissociation.** The conductivity of a solution is conditioned by the presence of ions, for the latter are the means by which the current is transported through the solution. Therefore, the greater the extent to which an electrolyte is dissociated in solution, the greater will be its conductivity; and, con-

versely, the greater the conductivity of a solution containing an equivalent weight of an electrolyte, the greater will be its dissociation. In the electrical conductivity of a solution, therefore, we have a ready means of determining the degree of dissociation. In practice the resistance of the solution is determined and from the latter the conductivity is readily calculated, the conductivity being the reciprocal of the resistance.

In conductivity determinations, the results are generally expressed on the basis of equivalent quantities.

The *specific resistance* of a solution is the resistance in ohms of a cube of one centimeter edge. The *specific conductivity* is the reciprocal of the specific resistance, and is therefore expressed in reciprocal ohms. The *molar conductivity* is the conductivity of a solution which contains the molecular weight of the substance in grams, contained between electrodes one centimeter apart. If, instead of the molecular weight, we use the equivalent weight\* in grams of the substance, we get the *equivalent conductivity*. If we denote the equivalent conductivity by  $\lambda$  (lambda) and the specific conductivity by  $\kappa$  (kappa), then we have  $\lambda = \kappa \times v$ , where  $v$  is the volume in cc. which contains the gram equivalent of the substance. An example will make this relation clear. Suppose we wish to find the conductivity of a 0.1 normal solution of HCl. We first determine the specific resistance, *i.e.*, the resistance of a 1 cm. cube of the solution when the latter is contained between two parallel electrodes. This is found to be 28.5 ohms. Its specific conductivity is therefore  $\frac{1}{28.5}$ , or 0.0351, reciprocal ohm. Since the solution is tenth normal, one equivalent will be contained in 10 liters, or 10,000 cc. Therefore  $\lambda = \text{equivalent conductivity} = 10,000 \times 0.0351 = 351$  reciprocal ohms.

The equivalent conductivity is found to increase with the dilution up to a certain point and then remains constant, so far as measurements show. At this point of maximum conductivity,

\* In the case of monobasic acids and their salts, the equivalent and molar conductivities will be identical. With dibasic acids and their salts, the equivalent will be one half of the molecular weight expressed in grams.

the electrolyte must be completely dissociated into its ions, and hence no increase in conductivity results on further dilution. The maximum conductivity is generally referred to as the *conductivity at infinite dilution* and is usually calculated from the curve representing the conductivities for known dilutions. Since the conductivity is proportional to the number of ions in solution, it follows that the ratio of the equivalent conductivity at a given dilution, to that at infinite dilution, will give us the percentage of the electrolyte that is ionized or the degree of dissociation at the given dilution; or  $\alpha = \frac{\mu_v}{\mu_\infty}$ , where  $\alpha$  denotes the degree of dissociation of the electrolyte at the dilution  $v$ ,  $\mu_v$  the equivalent conductivity at the dilution  $v$ , and  $\mu_\infty$  the equivalent conductivity at infinite dilution. An example will illustrate the application of the above principle.

The specific resistance of a HCl solution containing 1.825 grams of HCl per liter is found by experiment to be 55.55 ohms at + 18°.  $\kappa$  is therefore  $\frac{1}{55.55}$  reciprocal ohms. To calculate the value of  $\mu_\infty$ , we need only note that 1.825 g. HCl is  $\frac{1.825}{36.5}$ , or  $\frac{1}{20}$ , of a gram equivalent. Therefore  $v$ , the volume which will contain one gram equivalent (36.5 g.) of HCl, will be 20 liters, or 20,000 cc. Hence  $\mu_v = 20,000 \times \frac{1}{55.55} = 360$  reciprocal ohms.

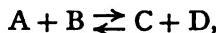
That is to say, the equivalent conductivity of such a solution is 360 reciprocal ohms. The equivalent conductivity of an HCl solution at infinite dilution at 18°, obtained by extrapolation from the curve of conductivities of known dilutions, is found to be 384 reciprocal ohms. Therefore  $\alpha = \frac{360}{384} = 93.75\%$ . That is to say, a solution containing 1.825 g. HCl per liter or a  $\frac{1}{20}$  molar solution of HCl, 93.75 % of the HCl is dissociated into H and Cl ions, while but 6.25 % is in the un-ionized condition.

In the following table are given the approximate values of the dissociation of the more common electrolytes met with in qualitative analysis:—

ACIDS	PERCENTAGE IONIZED IN 0.1 NORMAL SOLUTION
$\text{H}^+ \text{Cl}^-$ ; $\text{H}^+ \text{Br}^-$ ; $\text{H}^+ \text{I}^-$ ; $\text{H}^+ \text{NO}_3^-$	90
$\text{H}^+ \text{HSO}_4^-$	60
$\text{H}^+ \text{HC}_2\text{O}_4^-$	34
$\text{H}^+ \text{HSO}_3^-$	20
$\text{H}^+ \text{H}_2\text{PO}_4^-$	13
$\text{H}^+ \text{C}_2\text{H}_3\text{O}_2^-$	1.4
$\text{H}^+ \text{HCO}_3^-$	0.12
$\text{H}^+ \text{HS}^-$	0.05
$\text{H}^+ \text{CN}^-$	0.01
BASES	
$\text{K}^+ \text{OH}^-$ ; $\text{Na}^+ \text{OH}^-$	86
$\text{Ba}^+(\text{OH}^-)_2$	75
$\text{NH}_4^+ \text{OH}^-$	1.4
SALTS	
Type $\text{B}^+ \text{A}^-$ ( $\text{KNO}_3$ , $\text{KCl}$ )	84
Type $\text{B}_2^+ \text{A}^{--}$ or $\text{B}^{++} \text{A}_2^-$ ( $\text{K}_2\text{SO}_4$ , $\text{CaCl}_2$ )	73
Type $\text{B}_3^+ \text{A}^{---}$ or $\text{B}^{+++} \text{A}_3^-$ ( $\text{K}_3\text{Fe}(\text{CN})_6$ , $\text{FeCl}_3$ )	65
Type $\text{B}^{++} \text{A}^{--}$ ( $\text{MgSO}_4$ )	40
Pure water	0.00000002

## THE LAW OF MASS ACTION

In the following reversible reaction,



let us denote the concentrations \* of each of the substances by  $[\text{A}]$ ,  $[\text{B}]$ ,  $[\text{C}]$ , and  $[\text{D}]$  respectively. Let  $v$  represent the velocity with which A and B react to form C and D and  $v'$  the rate at which A and B are formed by the reaction between C and D. Experiment shows that, all other things being constant,  $v$  will be proportional to  $[\text{A}]$  and also to  $[\text{B}]$  and therefore to their product, or

$$v = k \times [\text{A}] \times [\text{B}],$$

\* These are expressed in moles per liter; thus a HCl solution containing 1.825 g. HCl per liter contains  $\frac{1.825}{36.5} = \frac{1}{20}$  mole; or 1 cc. contains 0.00005 mole.

where  $k$  is a constant dependent upon the nature of the substances reacting as well as upon the temperature. Similarly, the velocity of the reaction in the reverse direction, *i.e.*, the formation of A and B by the interaction of C and D may be represented by

$$v' = k' \times [C] \times [D].$$

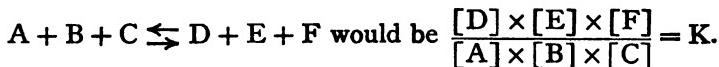
At equilibrium, the velocities in both directions will be equal; and we have therefore

$$v = v' \text{ or } k \times [A] \times [B] = k' \times [C] \times [D], \text{ or}$$

$$\frac{[C] \times [D]}{[A] \times [B]} = \frac{k'}{k} = K.$$

Expressed in words the above equation states that the product of the concentrations of the final substances, divided by the product of the concentrations of the initial substances, is a constant for any definite temperature for a reversible reaction.

Where three substances are involved on each side of the equation, the same principle applies. Thus the equation expressing the equilibrium for the reaction



If two combining weights of any substance take part in the reaction, then each is to be separately considered; thus the reversible reaction

$A + 2B \rightleftharpoons C + D$  may be written  $A + B + B \rightleftharpoons C + D$  ; and the equilibrium equation becomes

$$\frac{[C] \times [D]}{[A] \times [B]^2} = K.$$

In its most general form, the *law of mass action* as expressed in the above equation may be stated as follows: At any constant temperature, equilibrium will be reached in a reversible reaction, when the product of the concentrations of the final substances

divided by the product of the concentrations of the initial substances—each concentration raised to a power equal to the number of combining weights reacting—is a constant.

**The Mass Action Law and Ionization.** As the ionization of an electrolyte is a reversible reaction, we should expect that it would obey the law of mass action. Experiment shows, however, that while the mass action law rigidly applies to weak electrolytes, such as ammonium hydroxide and acetic acid, it does not apply, for reasons which still remain to be explained, to the dissociation of strongly ionized acids, bases, and salts.

An example will illustrate the application of the mass action law to ionization. A normal solution of ammonium hydroxide is found by experiment to ionize to the extent of 0.4 %. Ionization takes place according to the scheme



At equilibrium at a given temperature, we have

$$\frac{[\text{NH}_4^+] \times [\text{OH}^-]}{[\text{NH}_4\text{OH}]} = K. \quad (2)$$

Substituting the values in the above equation, we get

$$\frac{0.004 \times 0.004}{0.996} = 0.000016.$$

**Influence of Dilution.** Let us suppose that a normal solution of  $\text{NH}_4\text{OH}$  is diluted  $n$  times. Then the value of each of the concentrations in equation (2) will be reduced to  $\frac{1}{n}$  of its original magnitude, and we have

$$\frac{\frac{1}{n}[\text{NH}_4^+] \times \frac{1}{n}[\text{OH}^-]}{\frac{1}{n}[\text{NH}_4\text{OH}]} \text{ or } \frac{[\text{NH}_4^+] \times [\text{OH}^-]}{n[\text{NH}_4\text{OH}]} < K.$$

The fraction will no longer be equal to the equilibrium constant  $K$ , because the value of the denominator has been increased

$\pi$  times its original value. In order to restore the disturbed equilibrium, reaction (1) must proceed from left to right until, by an increase in the concentrations of  $\text{OH}^-$  and  $\text{NH}_4^+$  and a consequent decrease in the undissociated  $\text{NH}_4\text{OH}$ , the ratio again becomes equal to K. It is evident that the net result of the dilution is an increase in the dissociation.

**The Common Ion Effect.** The ionization of acetic acid is governed by the following equilibrium equation :—

$$\frac{[\text{H}^+] \times [\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = K.$$

Since a molar solution of acetic acid is ionized to the extent of 0.42 %, we have, substituting in the above equation,

$$\frac{0.0042 \times 0.0042}{0.9958} = 0.000018.$$

If to this solution we add 1 mole or 82 g. of  $\text{NaC}_2\text{H}_3\text{O}_2$  per liter, the salt being 53 per cent. dissociated, the concentration of the  $\text{C}_2\text{H}_3\text{O}_2^-$  ions would be increased to  $0.0042 + 0.53 = 0.5342$ . If we substitute this value in the above equation, we get  $\frac{0.0042 \times 0.534}{0.9958}$ , which is no longer equal to the equilibrium constant 0.000018, and as a consequence the equilibrium will be disturbed.

The equilibrium can be restored only by an adjustment of the values of the terms of the fraction. The denominator in the original equation for normal acetic acid when present alone (0.9958), is so near its maximal value that any increase in its magnitude (its highest possible value is 1) due to a combination of some of the  $\text{H}^+$  and  $\text{C}_2\text{H}_3\text{O}_2^-$  — to form undissociated  $\text{HC}_2\text{H}_3\text{O}_2$  — will be negligible. We therefore need only consider the concentrations of the ions in restoring equilibrium. The new value for the concentration of the  $\text{C}_2\text{H}_3\text{O}_2^-$  ions is  $\frac{0.534}{0.0042}$ , or 126 times as great as it was originally, and therefore to restore equilibrium, the other factor, the concentration of the hydrogen ions, must be reduced to  $\frac{1}{126}$  of its initial value; i.e.,

it will be reduced to  $\frac{1}{126} \times 0.0042 = 0.000034$ . The net effect of adding to a weakly dissociated acid a salt with an ion in common is to reduce the concentration of the hydrogen ions or to repress the ionization of the acid. A similar effect is produced when a salt with a common ion such as  $\text{NH}_4\text{Cl}$  is added to a weak base, such as ammonium hydroxide. The original concentration of the OH ions will be reduced by virtue of an increase in the concentration of the  $\text{NH}_4^+$  ions.

**Solubility Product.** In a saturated solution of  $\text{AgCl}$  equilibrium will be represented by the following equation:—

$$\frac{[\text{Ag}^+] \times [\text{Cl}^-]}{[\text{AgCl}]} = k \text{ or } [\text{Ag}^+] \times [\text{Cl}^-] = k \times [\text{AgCl}].$$

But since in a saturated solution  $[\text{AgCl}]$  is a constant, we may write the above equation in the form  $[\text{Ag}^+] \times [\text{Cl}^-] = K$ .

This equation states that for a saturated solution of a *difficultly soluble electrolyte*, the product of the concentrations of its ions is a constant for a given temperature. This product is called the *solubility product*.\*

With sparingly soluble electrolytes such as  $\text{AgCl}$  and  $\text{BaSO}_4$ , the dissociation of the dissolved substance may be regarded as complete so that the concentration of the ions will be equal to the solubility. An example will make this clear. The solubility of  $\text{AgCl}$  has been found to be 0.0000106 moles per liter. The solubility product will be therefore  $(0.0000106)^2$ .<sup>3</sup>

The application of the principle of the solubility product to precipitation may be stated as follows: Whenever the product of the concentrations of the ions, which by their union are capable of forming an insoluble substance, is greater than the solubility product of that substance, precipitation takes place. Conversely, when this product of the ionic concentrations is less than the solubility product of the insoluble substance, the latter, if present, will dissolve until this value is reached.

\* The principle of the solubility product cannot be applied to saturated solutions of soluble salts.

*Illustrations.* An aqueous solution of  $H_2S$  behaves as a weakly dissociated acid. The equilibrium equation is

$$\frac{[H^+]^2 \times [S^{--}]}{[H_2S]} = K.*$$

The addition of HCl to the solution will have the effect of increasing  $[H^+]$  and will correspondingly diminish  $[S^{--}]$  (common ion effect). Now if a solution of a copper salt to which some HCl be added † is treated with  $H_2S$ , a precipitate is thrown down. The formation of a precipitate is due to the fact that the solubility product of  $CuS$  is exceedingly small and that in spite of the repression of the ionization of the  $H_2S$  by the free HCl, the greatly diminished concentration of the S ions is still sufficient to yield with the Cu ions a value greater than the solubility product of  $CuS$ . On the other hand, if a zinc solution containing the same concentration of HCl be treated with  $H_2S$ , no precipitate of  $ZnS$  is obtained. The reason for this is that although the solubility product of  $ZnS$  is quite small, being much larger than that of  $CuS$ , the diminished concentration of the S ions occasioned by the presence of the HCl is far too low in value to cause the solubility product of  $ZnS$  to be exceeded, however great the concentration of the Zn ions may be. If, however, the solution be rendered alkaline, a precipitate of  $ZnS$  is at once obtained. The addition of the base not only neutral-

\* Hydrogen sulphide being a dibasic acid in solution ionizes as follows :—



The equilibrium equations for (1) and (2) are

$$\frac{[H^+] \times [HS^-]}{[H_2S]} = k_1 \quad \frac{[H^+] \times [S^{--}]}{[HS^-]} = k_2.$$

Multiplying these two equations together and cancelling, we get

$$\frac{[H^+]^2 \times [S^{--}]}{[H_2S]} = k_1 \times k_2 = K,$$

which is the equation given above.

† 2.5 cc. conc. HCl in a volume of 100 cc. of solution is a suitable concentration.

izes the HCl present, thus causing an increase in the concentration of the S ions, but the H<sub>2</sub>S itself is converted into an alkali sulphide whose degree of dissociation is vastly greater than that of H<sub>2</sub>S. This enormous increase in the concentration of the S ions accounts satisfactorily for the fact that in an alkaline solution the precipitation of zinc as sulphide by H<sub>2</sub>S is quantitative.

By an application of the principles involved in the solubility product and the "common ion effect," the student will readily comprehend why an excess of the reagent is required to effect a maximum precipitation of an ion. For example, in the precipitation of silver ions, it is customary to add an excess of chlorine ions. The latter will reduce the concentration of the silver ions to a negligible quantity and thus afford a practically complete precipitation.

The solubility of CaC<sub>2</sub>O<sub>4</sub> in an excess of HCl may be explained from the standpoint of the ionic theory and solubility product principle as follows: Experiment shows that oxalic acid is a weakly dissociated acid; hydrochloric acid, on the other hand, is a strongly ionized acid. In consequence of this difference, the tendency, where the ions of both acids are in solution, will be for the weakly dissociated acid to form. In the case under consideration, some of the hydrogen ions from the HCl will unite with some of the C<sub>2</sub>O<sub>4</sub><sup>2-</sup> ions derived from the CaC<sub>2</sub>O<sub>4</sub> in solution, to form the weakly dissociated oxalic acid. The removal of C<sub>2</sub>O<sub>4</sub><sup>2-</sup> ions from the solution will cause the product of the concentrations of the Ca and C<sub>2</sub>O<sub>4</sub><sup>2-</sup> ions in solution to fall below the solubility product of CaC<sub>2</sub>O<sub>4</sub>. In consequence more CaC<sub>2</sub>O<sub>4</sub> will go into solution in order to restore equilibrium; and this process of the removal of C<sub>2</sub>O<sub>4</sub><sup>2-</sup> by the H ions, and the solution of the CaC<sub>2</sub>O<sub>4</sub>, will go on until all the CaC<sub>2</sub>O<sub>4</sub> is dissolved. The reaction may be represented as follows:—



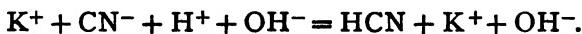
**Hydrolysis.** While the concentrations of OH and H ions in water is exceedingly small, there being only  $\frac{1}{1000000}$  of a mole for each of these ions in a liter of water, they must be taken into account in dealing with the behavior of solutions of

salts formed by the union of a weak base with a strong acid, and *vice versa*. Thus the student has already become familiar with the fact that aqueous solutions of  $\text{Na}_2\text{CO}_3$  and  $\text{KCN}$  possess an alkaline reaction, while solutions of  $\text{FeCl}_3$  and  $\text{CuSO}_4$  are acid to litmus. In the former case the reaction is due to the presence of  $\text{OH}$  ions, while in the latter case the acidity is occasioned by the presence of  $\text{H}$  ions in solution.

When potassium cyanide is dissolved in water, it dissociates to a considerable extent into  $\text{K}$  and  $\text{CN}$  ions. We have, therefore, in solution for the moment  $\text{K}^+$ ,  $\text{CN}^-$ ,  $\text{H}^+$ , and  $\text{OH}^-$ . Now on encountering the  $\text{CN}$  ions, the  $\text{H}$  ions will combine with them, forming the very feebly dissociated acid  $\text{HCN}$ . The removal of  $\text{H}$  ions from the solution will cause more water to dissociate into  $\text{H}$  and  $\text{OH}$  ions; the former will again be taken up by more  $\text{CN}$  ions, and this process will continue until the equilibrium constant for  $\text{HCN}$  is reached, *i.e.*, until

$$\frac{[\text{H}^+] \times [\text{CN}^-]}{[\text{HCN}]} = K.$$

The removal of the  $\text{H}$  ions from the solution will result in the accumulation of  $\text{OH}$  ions, and these will give to the solution its alkaline reaction. The reaction may therefore be represented as follows:—

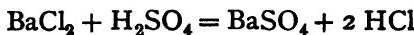


It is evident that the  $\text{OH}$  ions will not combine with the  $\text{K}$  ions for the reason that  $\text{KOH}$ , even if formed, would be largely dissociated in aqueous solution.

By a similar process of reasoning it may be shown why an aqueous solution of  $\text{FeCl}_3$  possesses an acid reaction. In this case, the weakly dissociated base  $\text{Fe}(\text{OH})_6$  is formed, which removes the  $\text{OH}$  ions from the solution, thus causing an accumulation of  $\text{H}$  ions from the progressive dissociation of water. The final solution, therefore, will possess an acid reaction. We may define *hydrolysis* as the process by which a salt of a weak acid or base is decomposed into its corresponding acid and base by the action of water.

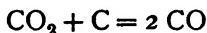
### EQUATIONS

A chemical equation is a shorthand means of expressing a reaction. The equation



gives us, first, the qualitative fact that when  $\text{BaCl}_2$  solution is treated with  $\text{H}_2\text{SO}_4$ , a precipitate of  $\text{BaSO}_4$  is formed, together with hydrochloric acid; and, second, the quantitative relations between the substances reacting — namely, that 137 parts by weight of barium in solution will require 98 parts by weight of  $\text{H}_2\text{SO}_4$  for its complete precipitation; or that  $(137 + 70)$  parts by weight of  $\text{BaCl}_2$ , when treated with 98 parts of  $\text{H}_2\text{SO}_4$ , yield  $(137 + 96)$  parts by weight of  $\text{BaSO}_4$  and  $(2 \times 36.5)$  parts by weight of HCl.

In the case of gases, equations give us, besides qualitative and quantitative relations, those of volume also. The equation



states that when one volume of  $\text{CO}_2$  is reduced by the agency of carbon, two volumes of carbon monoxide are produced.

Before writing an equation, we must first know the *facts*. True, we may reason by analogy and foretell a reaction, and at once write its equation; but such equations are to be looked upon with doubt until verified by actual experimentation. Briefly, then, to write an equation, we must know the formulas of the substances entering into the reaction, sometimes called the *factors* and appearing on the left side of the equality sign, and also we must know one or more of the essential *products*. All of the latter need not be known; they can, with a little knowledge, be "worked out." It is a good plan to designate by means of an arrow pointing downward the formulas of insoluble substances and with an arrow pointing upward the formulas of gases; *e.g.*, a glance at the equation



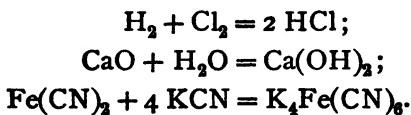
shows that  $\text{CaCO}_3$  is a solid, that  $\text{CO}_2$  is a gas, and that the other substances are in solution. Any determined method,

however, will answer the purpose, and as a rule it is applied only to the products of a reaction.

The *Law of the Conservation of Weight* states that during a chemical change there is no loss or gain in weight. From this it follows that the total weight of the factors must be equal to the total weight of the products. The *Law of the Conservation of Elements* states the immutability of the elements during chemical change. From the combination of these two fundamental laws of chemistry, it follows that *in any chemical equation, the same number of combining weights of each element must appear on both sides.* This last rule, with a knowledge of the formulas of the factors and products, suffices for the writing of an equation. One need not attempt to remember the coefficients appearing in chemical equations, but should invariably work them out. The method of doing this will be explained later in connection with the writing of a number of rather complex equations given under "Oxidation and Reduction."

#### TYPES OF REACTIONS

Reactions may be classed under three heads, viz. **synthesis**, **analysis**, and **metathesis**. A synthetic reaction is one in which a compound is formed from its elements, or, in general, a more complex compound formed by the union of simpler ones, thus:—



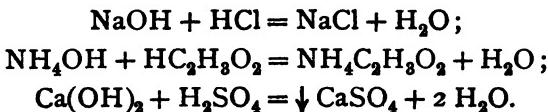
An analytical reaction is one in which some complex compound is broken down into its elements or into simpler compounds; for example:—



A metathetical reaction is one in which there is an exchange of radicals; these represent by far the largest number met with in qualitative analysis; for example:—

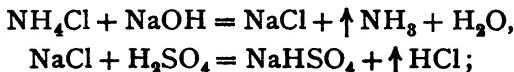
- (a)  $\text{AgNO}_3 + \text{HCl} = \downarrow \text{AgCl} + \text{HNO}_3$ ;  
 (b)  $\text{Cu}(\text{NO}_3)_2 + \text{H}_2\text{S} = \downarrow \text{CuS} + 2 \text{HNO}_3$ ;  
 (c)  $\text{BaCl}_2 + \text{H}_2\text{SO}_4 = \downarrow \text{BaSO}_4 + 2 \text{HCl}$ .

Neutralization of bases by acids comes under this head.



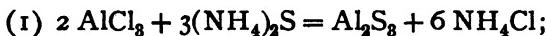
In some cases it is necessary to know the conditions under which the reaction takes place before the equation can be written; for example, if copper nitrate is mixed with dilute  $\text{H}_2\text{SO}_4$ , no apparent reaction takes place, but if the mixture is boiled till  $\text{SO}_3$  fumes are given off, the following reaction occurs:—  $\text{Cu}(\text{NO}_3)_2 + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + \uparrow 2 \text{HNO}_3$ .

Similarly, on boiling, the following reactions will take place:—

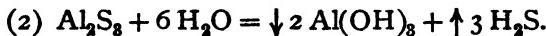


for, at these temperatures,  $\text{HCl}$ ,  $\text{NH}_3$ , and  $\text{HNO}_3$  are evolved as gases.

In writing a complicated equation, it is convenient to consider the reaction as taking place in several stages; \* thus, when ammonium sulphide is added to an aqueous solution of  $\text{AlCl}_3$ , a precipitate consisting of the hydroxide and not the sulphide is obtained, and at the same time the evolution of  $\text{H}_2\text{S}$  takes place. This reaction becomes easily comprehended if we consider it as taking place in two stages, viz.:—



but as  $\text{Al}_2\text{S}_3$  does not exist in contact with water, it decomposes according to the equation



\* Since we do not know what causes chemical activity, the exact mechanism of a reaction is unknown and is perhaps unknowable; any device tending to elucidate or simplify a complicated reaction, it is believed, should be utilized, although experimental proof for these devices cannot always be supplied.

Combining (1) and (2), and eliminating  $\text{Al}_2\text{S}_3$ , which appears on opposite sides of the equations, we get as the final equation  $2 \text{AlCl}_3 + 3(\text{NH}_4)_2\text{S} + 6 \text{H}_2\text{O} = \downarrow 2 \text{Al}(\text{OH})_3 + 6 \text{NH}_4\text{Cl} + \uparrow 3 \text{H}_2\text{S}$ . Still more complicated equations will be met with which can be readily written, if first resolved into two or more single equations, and the latter are then combined into one equation with the elimination of common terms.

### OXIDATION AND REDUCTION

**Oxidation** may be defined as a chemical change in which oxygen or some other electro-negative element or radical is added, or hydrogen or some other electro-positive element or radical is removed. **Reduction** is the reverse process. The substance which effects the oxidation is called the **oxidizing agent**; and that causing the reduction is called the **reducing agent**. A consideration of the following examples will make the matter clear:—

#### Oxidation:

- (1)  $2 \text{FeO} + \text{O} = \text{Fe}_2\text{O}_3$ ;
- (2)  $\text{FeCl}_2 + \text{Cl} = \text{FeCl}_3$ ;
- (3)  $2 \text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{Br}_2 = \text{Fe}_2(\text{SO}_4)_3 + 2 \text{HBr}$ ;
- (4)  $\text{SnCl}_2 + 2 \text{HgCl}_2 = \text{SnCl}_4 + \downarrow 2 \text{HgCl}$ .

#### Reduction:

- (5)  $\text{CuO} + \text{H}_2 = \text{Cu} + \text{H}_2\text{O}$ ;
- (6)  $2 \text{FeCl}_3 + \text{SnCl}_2 = 2 \text{FeCl}_2 + \text{SnCl}_4$ ;
- (7)  $\text{Fe}_2(\text{SO}_4)_3 + \text{H}_2^* = 2 \text{FeSO}_4 + \text{H}_2\text{SO}_4$ ;
- (8)  $2 \text{HgCl}_2 + \text{SnCl}_2 = \downarrow 2 \text{HgCl} + \text{SnCl}_4$ .

The first four equations represent oxidation reactions, for in each case oxygen or some other electro-negative element or radical has been added. The last four are types of reduction processes, for in each case oxygen or some other electro-nega-

\* The hydrogen is generated in contact with the  $\text{Fe}_2(\text{SO}_4)_3$  by the action of a metal on an acid.

tive element or group has been removed. If we leave out of consideration those simple cases of oxidation and reduction in which there is a direct addition of the oxidizing or reducing agent with the production of a single product, as in (1) and (2), and carefully examine the others, we find that in every case oxidation is accompanied by reduction, the oxidation of one substance always involving the reduction of another; thus, in example (4), the oxidation of  $\text{SnCl}_2$  has been accomplished at the expense of the  $\text{HgCl}_2$ , which has been reduced at the same time to  $\text{HgCl}$ . In (5) the reduction of  $\text{CuO}$  has been simultaneous with the oxidation of  $\text{H}$  to  $\text{H}_2\text{O}$ . Similarly, in (6) the reduction of  $\text{FeCl}_3$  has been accompanied by the oxidation of  $\text{SnCl}_2$  to  $\text{SnCl}_4$ .

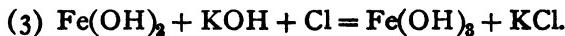
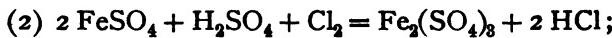
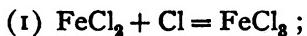
Further examination of the above eight examples of oxidation and reduction shows that oxidation is accompanied by an increase in valence, while in reduction reactions, a lowering of valence is observed; thus, in (4) the valence of Sn has been increased from 2 to 4, while at the same time the valence of Hg has been lowered from 2 to 1. In general, we may say that any reaction in which there is an increase in valence is one of oxidation, while a reaction in which there is a lowering of valence is one of reduction.

#### OXIDIZING AGENTS

The principal oxidizing agents are: oxygen, the halogens,  $\text{HNO}_3$ , *aqua regia*,  $\text{KClO}_3$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{KMnO}_4$ ,  $\text{Na}_2\text{O}_2$ ,  $\text{H}_2\text{O}_2$ , and  $\text{PbO}_2$ .

The chief reducing agents are: nascent H,  $\text{SnCl}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{SO}_3$ ; and, at elevated temperatures, C,  $\text{KCN}$ , and organic matter.

The halogens either add directly (1); or else may be regarded as oxidizing the acid by removing the H, setting free the acid radical, which then adds on (2); or with bases by removing the metal and thus leaving the hydroxyl radical ( $\text{OH}$ ) to add on (3). Examples of such changes follow.



Nitric acid acts as an oxidizing agent by virtue of its ready decomposition according to the equation



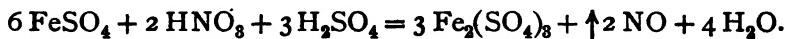
From this it is evident that 2 formular weights of  $\text{HNO}_3$  yield 3 combining weights of O. The liberated O may be regarded as acting indirectly in the same way as Cl; that is, by oxidizing the H of the acid and liberating the acid radical, which then adds on, thus :—

- $$(1) 2 \text{HNO}_3 = 2 \text{NO} + \text{H}_2\text{O} + 3 \text{O};$$
- $$(2) 3 \text{H}_2\text{SO}_4 + 3 \text{O} = 3 \text{H}_2\text{O} + 3 \text{SO}_4.$$

Since 2 formular weights of  $\text{FeSO}_4$  require one  $\text{SO}_4$  for complete oxidation, and since 3  $\text{SO}_4$  radicals are made available by 2  $\text{HNO}_3$ , it follows that 2 formular weights of  $\text{HNO}_3$  will oxidize 6  $\text{FeSO}_4$ , to wit :—



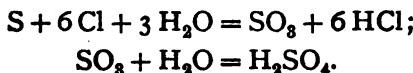
Adding (1), (2), and (3), and eliminating the factors appearing on both sides in the equations, as 3 O and 3  $\text{SO}_4$ , the final equation becomes —



*Aqua regia* is not only a good solvent but is also an excellent oxidizing agent. Its action is practically the same as that of Cl. It is prepared by mixing 1 part of  $\text{HNO}_3$  with 3 parts of HCl. When heated alone, it is said to yield  $\text{NOCl}$  and Cl, according to the equation  $3 \text{HCl} + \text{HNO}_3 = \text{NOCl} + \text{Cl}_2 + 2 \text{H}_2\text{O}$ ; but in the presence of an oxidizable substance all of the Cl is available, so that the equation with *aqua regia* may be written as follows :—



If the action of *aqua regia* on a sulphide is long continued, the liberated S will be partially or entirely oxidized to  $\text{H}_2\text{SO}_4$  :—



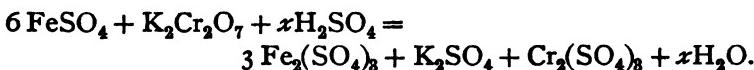
Potassium chlorate,  $\text{KClO}_3$ , when used in conjunction with  $\text{HCl}$ , is a powerful oxidizing agent. In effect it is similar to *aqua regia* and chlorine, as the following equations will indicate:—

- (1)  $2 \text{KClO}_3 + 2 \text{HCl} = 2 \text{HClO}_3 + 2 \text{KCl};$
- (2)  $2 \text{HClO}_3 = \text{H}_2\text{O} + 2 \text{ClO}_2 + \text{O};$
- (3)  $2 \text{HCl} + \text{O} = \text{H}_2\text{O} + \text{Cl}_2.$

Adding (1), (2), and (3), we get the following:—

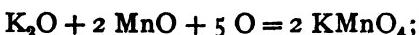


Potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ , contains the acid anhydride  $\text{CrO}_3$ ; its composition may be represented by the formula  $2 \text{CrO}_3 + \text{K}_2\text{O}$ . As  $2 \text{CrO}_3$  will, on reduction, yield  $\text{Cr}_2\text{O}_8 + 3 \text{O}$ , it is evident that one formular weight of  $\text{K}_2\text{Cr}_2\text{O}_7$  possesses the same oxidizing power as two formular weights of  $\text{HNO}_3$ , both yielding 3 combining weights of O. We therefore obtain the following equation for the oxidation of ferrous sulphate by  $\text{K}_2\text{Cr}_2\text{O}_7$ :—



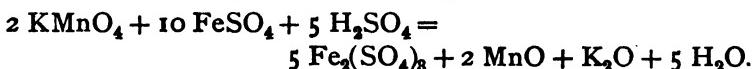
The reduction of  $2 \text{CrO}_3$  to  $\text{Cr}_2\text{O}_8$  leaves the latter, as well as  $\text{K}_2\text{O}$ , behind. These basic oxides readily dissolve in  $\text{H}_2\text{SO}_4$  with the formation of sulphates which appear in the above equation. The amount of  $\text{H}_2\text{SO}_4$  needed to balance the above reaction may be calculated from the following considerations:  $\text{Cr}_2\text{O}_8$  requires 3 formular weights of  $\text{H}_2\text{SO}_4$  for its solution;  $\text{K}_2\text{O}$  requires 1, thus making a total of 4. In addition to this quantity, we must consider the amount necessary to react with the 3 combining weights of O derived from the  $2 \text{CrO}_3$ ; this will require 3 more  $\text{H}_2\text{SO}_4$ , making the total 7, which becomes the coefficient of  $\text{H}_2\text{SO}_4$  in the above equations. We should also have 7  $\text{H}_2\text{O}$  in the right-hand member of the equation for a reason which must be evident to the reader.

Potassium permanganate,  $\text{KMnO}_4$ , behaves in acid solution as

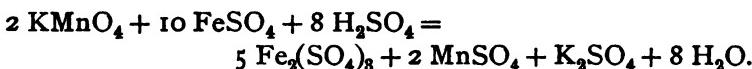


that is,  $2 \text{KMnO}_4$  yields 5 combining weights of O.

The equation for the oxidation of ferrous sulphate by  $\text{KMnO}_4$  may be written from the following considerations: 5 combining weights of O will liberate 5  $\text{SO}_4$  radicals; but as one  $\text{SO}_4$  suffices for the oxidation of 2  $\text{FeSO}_4$ , it is evident that 2  $\text{KMnO}_4$  will oxidize 10  $\text{FeSO}_4$ , and we get the equation —



However,  $\text{K}_2\text{O}$  and 2  $\text{MnO}$  readily dissolve in  $\text{H}_2\text{SO}_4$  with the formation of sulphates; three additional formular weights of  $\text{H}_2\text{SO}_4$  must therefore be added to the above equation, together with 3 formular weights of water produced by the solution of the oxides in the acid. The final equation becomes —



Sodium dioxide,  $\text{Na}_2\text{O}_2$ , acts as an oxidizing agent by virtue of its instability in water or when it is heated in the presence of an oxidizable substance in consequence of which it gives off oxygen :—  $\text{Na}_2\text{O}_2 + \text{H}_2\text{O} = 2 \text{NaOH} + \text{O}$ .

A solution of hydrogen dioxide,  $\text{H}_2\text{O}_2$ , also serves as an oxidizing agent for the same reason :—



$\text{Na}_2\text{O}_2$  is, however, preferable to  $\text{H}_2\text{O}_2$ , for the latter can only be safely\* used in diluted form (3%), while the former can be used in any concentration.  $\text{Na}_2\text{O}_2$  has the further advantage of supplying at the same time sodium hydroxide. For oxidation in alkaline media, therefore,  $\text{Na}_2\text{O}_2$  is the better reagent.

Lead dioxide,  $\text{PbO}_2$ , like  $\text{Na}_2\text{O}_2$ , yields O according to the equation —



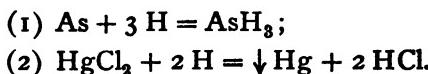
It is employed to effect oxidation in acid media; as in the conversion of  $\text{MnO}$  to  $\text{HMnO}_4$ ; the  $\text{PbO}$  is converted by the excess of acid present into a salt.

\* A 30% solution has recently become very useful in the laboratory, especially in the hands of experienced chemists. We regard the above statement as particularly applicable to student work.

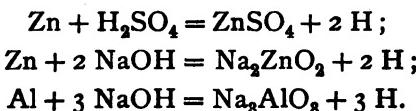
### REDUCING AGENTS

Any oxidizable substance can be utilized as a reducing agent, since, in order to reduce, it must be capable of oxidation.

Nascent H \* acts as a reducing agent by either adding itself directly (1) or by its ability to unite with, and thus remove, the halogens contained in the compound (2):—

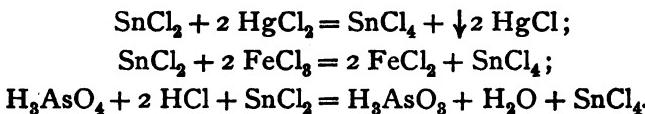


Nascent H may be prepared by the action of an acid or alkali on certain metals :—

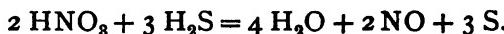


Nascent H may therefore be employed in both acid and alkaline media.

Stannous chloride,  $\text{SnCl}_2$ , acts as a reducing agent, preferably in an acid solution, by virtue of the ease with which it readily oxidizes to  $\text{SnCl}_4$ :—



Hydrogen sulphide,  $\text{H}_2\text{S}$ , by virtue of the readiness with which it decomposes into H and S is a reducing agent. The hydrogen acts as nascent hydrogen, while the sulphur separates out in the solid state. Nearly all oxidizing agents are reduced by  $\text{H}_2\text{S}$  with the separation of sulphur, thus :—

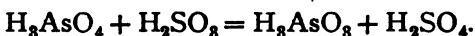


Hence, sulphides soluble in  $\text{HNO}_3$ , like those of Pb, Bi, and Cu, do not liberate  $\text{H}_2\text{S}$ , because the latter at once acts on the

\* Nascent H is used here to designate the hydrogen which is formed when the acid and metal or alkali and metal are both in contact with the solution to be reduced.

excess of  $\text{HNO}_3$  present with the liberation of S, as indicated in the equation above. Halogens, *aqua regia*, ferric salts, potassium permanganate, and chromates are also reduced by  $\text{H}_2\text{S}$  with the separation of S, and, in some cases, with a change in color of the solution (see pp. 60-61).

Sulphurous acid,  $\text{H}_2\text{SO}_3$ , and the sulphites easily remove oxygen from compounds with the formation of sulphuric acid and sulphates respectively, thus :—

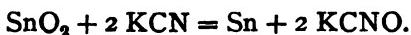


While  $\text{H}_2\text{SO}_3$  is an excellent reducing agent for arsenic when in the pentavalent condition, it cannot be used in a complete analysis if the alkaline earths are known to be present, because of the formation of  $\text{H}_2\text{SO}_4$  as one of the products of the reduction. The reduction of arsenic compounds with  $\text{H}_2\text{SO}_3$  is best accomplished in a pressure bottle at  $100^\circ\text{C}$ .

Carbon acts as a reducing agent by virtue of its ability to oxidize to CO and  $\text{CO}_2$ , thus :—



The use of potassium cyanide, KCN, as a reducing agent in the "dry way" depends upon its ability to take up O and form KCNO :—



### CLASSIFICATION

In the analysis of a solution for metals, it has been found convenient to first separate them into groups by the use of certain reagents known as **group reagents**.

If to a solution containing all the metals in the form of salts we add a slight excess of dilute hydrochloric acid, a precipitate consisting of the chlorides of silver, mercury (-ous), and lead will form. These metals are classed together and designated as the **first group**. If, now, the precipitate of the chlorides of the first group is filtered off and the filtrate, which is acid from the excess of HCl used, is treated with a stream of  $\text{H}_2\text{S}$  gas, there

will form a precipitate consisting of the sulphides of mercury (ic), lead,\* bismuth, copper, cadmium, arsenic, antimony, and tin. These metals are therefore classed together and collectively are known as the **second group**. If the filtrate from the second group is rendered alkaline with ammonium hydroxide,† and then ammonium sulphide is added, a precipitate of the hydroxides of aluminum and chromium, together with the sulphides of iron, nickel, cobalt, manganese, and zinc, will form. These constitute the **third group**. The filtrate from this group will contain an excess of  $\text{NH}_4\text{OH}$  and some  $\text{NH}_4\text{Cl}$ ,† in addition to all the metals not included in the previous three groups. If to this filtrate we add ammonium carbonate in slight excess, a precipitate consisting of the carbonates of barium, strontium, and calcium will form; these constitute the **fourth group**. The final filtrate will contain all the other metals not precipitated by the previous group reagents; they are magnesium, sodium, potassium, and ammonium, and these form the **fifth group**.‡

The division of the metals into groups is thus seen to depend upon their behavior, when in solution, towards certain reagents added in a certain order. If we were to use different reagents, the grouping would be different. It is equally important to remember that the *order* of the addition of the reagents is as vital for the above classification as the *choice* of the reagents; for if we were to reverse the order,—*i.e.*, begin with  $\text{NH}_4\text{OH}$ , then add  $(\text{NH}_4)_2\text{CO}_3$  and then  $(\text{NH}_4)_2\text{S}$ ,—we should get quite a different classification. It is furthermore to be noted that each reagent, taken in the order given, is capable of separating its own group from those which *follow* and not from those which

\* Since  $\text{PbCl}_2$  is somewhat soluble in water, some of it will pass into the filtrate from Group I. and will be precipitated in the second group as sulphide. Pb, therefore, belongs to both groups.

† When the solution which is acid with HCl is rendered alkaline with ammonium hydroxide,  $\text{NH}_4\text{Cl}$  forms; the presence of this salt prevents magnesium from precipitating along with the metals of Group III. For the same reason, magnesium is not thrown down in the fourth group.

‡ The rarer metals are not considered in the text. Special treatises more or less elaborate are necessary when they are included.

*precede* it in the regular order. Below is given in tabular form the separation of the metals into groups with the formulas of the compounds which are formed.

Solution containing all the metals in the form of salts. Add HCl and filter.

Precipitate : AgCl, PbCl <sub>2</sub> , HgCl. Group I.	Filtrate: Groups II.-V. + excess HCl ; pass in H <sub>2</sub> S and filter.		
Precipitate : HgS, PbS, Bi <sub>2</sub> S <sub>3</sub> , CuS, CdS, As <sub>2</sub> S <sub>3</sub> , Sb <sub>2</sub> S <sub>3</sub> , SnS. Group II.	Filtrate: Groups III.-V. + HCl + H <sub>2</sub> S ; make alkaline with NH <sub>4</sub> OH, add (NH <sub>4</sub> ) <sub>2</sub> S and filter.		
Precipitate : Al(OH) <sub>3</sub> , Cr(OH) <sub>3</sub> , FeS, NiS, CoS, MnS, ZnS. Group III.	Precipitate : BaCO <sub>3</sub> , SrCO <sub>3</sub> , CaCO <sub>3</sub> , Group IV.	Filtrate: Groups IV.-V. + NH <sub>4</sub> Cl ; add (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> and filter.	Filtrate: contains Mg, Na, K, NH <sub>4</sub> . Group V.

It is thus seen that —

**Group I.** includes those metals whose chlorides are insoluble in water and in dilute acids, and are hence precipitated by HCl.

**Group II.** includes those metals which are not precipitated by HCl, but whose sulphides are precipitated by H<sub>2</sub>S in acid solutions. The sulphides are, therefore, insoluble in water and in dilute acids.

**Group III.** includes those metals which are not precipitated either by HCl or H<sub>2</sub>S in acid solution, but are precipitated by (NH<sub>4</sub>)<sub>2</sub>S in solutions alkaline with NH<sub>4</sub>OH and in the presence of NH<sub>4</sub>Cl.

**Group IV.** includes those metals unprecipitated by the reagents of Groups I., II., III., but which are precipitated by (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> in the presence of NH<sub>4</sub>Cl.

**Group V.** includes metals not precipitated by the reagents of Groups I.-IV.



## PART I

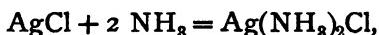
### THE METALS

#### Reactions of the Metals of Group I

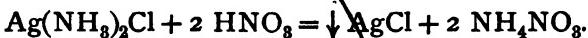
THE metals, silver, mercury (-ous), and lead, comprising this group, are distinguished from all others by the insolubility of their chlorides in water and in dilute acids. With the exception of the nitrates and acetates, which are colorless, nearly all the salts of the metals of this group are insoluble in water.

#### SILVER

1. Hydrochloric acid or a soluble chloride, when added to solutions of silver salts, gives a white, curdy precipitate of silver chloride ( $\text{AgCl}$ ) which darkens on exposure to light. The precipitate is insoluble in water, the solubility being approximately 1 part in 700,000 parts of water; it is insoluble in dilute acids and in dilute *aqua regia*, but is somewhat soluble in concentrated acids. Ammonium hydroxide readily dissolves it, with the formation of silver ammonia chloride [ $\text{Ag}(\text{NH}_3)_2\text{Cl}$ ]:—



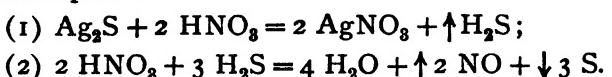
from which  $\text{AgCl}$  reprecipitates on acidification with nitric acid:—



Silver chloride also dissolves in solutions of potassium cyanide and sodium thiosulphate; when cautiously heated, it fuses without decomposition.

2. Hydrogen Sulphide and soluble sulphides precipitate black  $\text{Ag}_2\text{S}$ , insoluble in cold dilute acids, alkali hydroxides, and alkali sulphides; it is soluble in hot dilute  $\text{HNO}_3$ , with the formation of  $\text{AgNO}_3$  and separation of sulphur. The reaction can be con-

sidered as taking place in two steps, the first consisting of the solution of the sulphide with the liberation of  $H_2S$  and the second of the oxidation of the  $H_2S$  by the excess of  $HNO_3$  present with the formation of water, nitric oxide, and the separation of sulphur :—



Multiplying equation (1) by 3 and adding it to (2), with the elimination of 3  $H_2S$ , which appears on opposite sides, we get as a final result :—



Other insoluble compounds of silver are :—

$AgBr$  — yellowish white;  $AgI$  — pale yellow;  $AgCN$  — white;  $Ag_2O$  — brown.

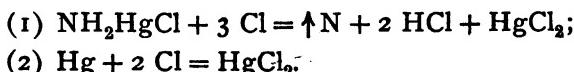
Silver is readily precipitated from its solutions by the more electro-positive metals, as  $Cu$ ,  $Zn$ ,  $Hg$ , and  $Fe$ , as well as by various reducing agents.

### MERCURY (-ous)

i. Hydrochloric acid and soluble chlorides give with solutions of mercurous salts a white precipitate of  $HgCl$  (calomel), insoluble in water, the solubility being about 1 part in 300,000; it is insoluble in cold dilute acids, but dissolves in strong nitric acid and in *aqua regia*, the latter oxidizing it to  $HgCl_2$ . Ammonium hydroxide converts calomel into a black mixture of finely divided mercury and  $NH_2HgCl$ , insoluble in excess of the reagent (this is the most characteristic reaction for mercurous salts):—



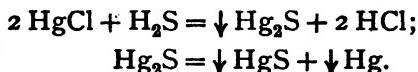
The black mixture dissolves in *aqua regia* with the formation of mercuric chloride :—



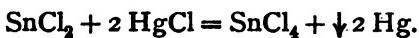
Adding (1) and (2), we get



2. Hydrogen Sulphide gives with solutions of mercurous salts a black precipitate consisting of a mixture of mercuric sulphide and elementary mercury; it may be assumed that the mercurous sulphide which forms first, decomposes on account of its instability, thus:—



3. Reducing Agents, as  $\text{FeSO}_4$  or  $\text{SnCl}_2$ , rapidly reduce mercurous salts to metallic mercury:—

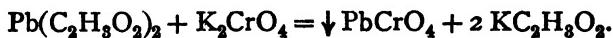


### LEAD

1. Hydrochloric acid and soluble chlorides give with solutions of lead salts, which are not too dilute, a white precipitate of  $\text{PbCl}_2$ , soluble in 100 parts of cold and 25 parts of boiling water; from the latter on cooling,  $\text{PbCl}_2$  separates out in the form of needles.  $\text{PbCl}_2$  is much more insoluble in dilute HCl than in water. Ammonium hydroxide changes it to a basic chloride  $[\text{Pb}(\text{OH})\text{Cl}]$  which is extremely insoluble in water.

2. Dilute sulphuric acid and soluble sulphates precipitate white  $\text{PbSO}_4$  which is practically insoluble in  $\text{H}_2\text{O}$  (1 part in about 30,000), but much more insoluble in the presence of dilute  $\text{H}_2\text{SO}_4$  or alcohol. It is soluble to some extent in  $\text{HNO}_3$ , and is completely soluble in fixed alkalies and in a hot strong solution of  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ ; from these solutions  $\text{PbSO}_4$  is reprecipitated on adding  $\text{H}_2\text{SO}_4$ .

3. Potassium Chromate ( $\text{K}_2\text{CrO}_4$ ) precipitates yellow lead chromate, readily soluble in sodium hydroxide, but insoluble in  $\text{NH}_4\text{OH}$  and acetic acid:—

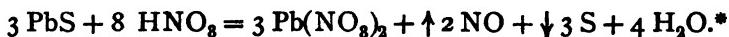


4. Hydrogen Sulphide from slightly acid solutions of lead salts precipitates black  $\text{PbS}$ . In the presence of much HCl,  $\text{H}_2\text{S}$  either fails to precipitate or else produces a red insoluble com-

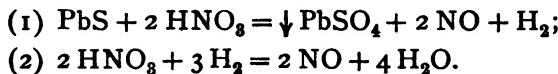
pound of the formula  $\text{PbCl}_2 \cdot 2 \text{ PbS}$ ; the latter is converted into black  $\text{PbS}$  by treatment with  $(\text{NH}_4)_2\text{S}$  or by diluting the solution and passing in more  $\text{H}_2\text{S}$ . Lead sulphide is insoluble in dilute acids, alkali hydroxides, and alkali sulphides. Hot dilute  $\text{HNO}_3$  dissolves it with the formation of the nitrate and separation of sulphur. Hot concentrated  $\text{HNO}_3$  oxidizes it to sulphate.



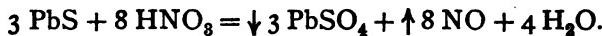
With dilute  $\text{HNO}_3$  this reaction occurs:—



With concentrated  $\text{HNO}_3$ , the reactions may be represented by the following equations:—

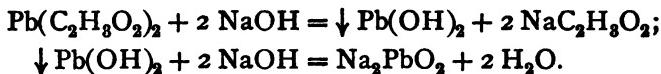


Multiplying (1) by 3 and adding it to (2) with the elimination of 3  $\text{H}_2$ , we get —



In a neutral solution containing 1 part of  $\text{Pb}$  in 100,000 parts of water,  $\text{H}_2\text{S}$  will distinctly reveal its presence.  $\text{H}_2\text{S}$  is, therefore, an exceedingly sensitive reagent for the detection of  $\text{Pb}$ .

**5. Sodium or Potassium Hydroxide** precipitates white  $\text{Pb}(\text{OH})_2$ , soluble in excess:—



**6. Ammonium Hydroxide** precipitates a basic salt, insoluble in excess.

Other difficultly soluble compounds of  $\text{Pb}$  are:—

$\text{PbI}_2$  — yellow;  $\text{PbBr}_2$  — white;  $\text{PbSO}_4$  — white; basic carbonate — white,  $2 \text{ PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ ;  $\text{PbC}_2\text{O}_4$  — white.

\* Resolvable into two steps, as in the case of the solution of  $\text{Ag}_2\text{S}$  in  $\text{HNO}_3$ .

## GROUP I

## Outline of the Process of Analysis

An examination of the foregoing reactions shows that all the metals of this group may be precipitated by HCl. By filtering off this precipitate, we should have on the filter a mixture consisting of the chlorides of Ag, Hg (-ous), and Pb. In order to identify the components of this mixture, it is first necessary to effect their separation; this can be accomplished by taking advantage of the difference of their behavior towards hot water and ammonium hydroxide.  $PbCl_2$  is completely soluble in hot water, while the others are practically insoluble. It is thus possible, by treating the mixed chlorides with a sufficient amount of hot water, to dissolve, or extract, the  $PbCl_2$ . If the quantity of Pb is large, the hot aqueous extract on cooling will deposit the characteristic needles of  $PbCl_2$ , and thus the presence of Pb may be proved. If the amount is small, the water extract will require further testing to prove that it contains Pb. The tests with  $H_2SO_4$  and  $K_2CrO_4$  will prove conclusively whether or not lead has been extracted and therefore its presence in the original solution.

Having extracted all the Pb, the residue on the filter may consist of the chlorides of Ag and Hg. These can be readily separated by reason of the solubility of the former in ammonium hydroxide; so that on treating the residue on the filter with this reagent we should obtain a filtrate and a residue. The former (if Ag is present) will contain the Ag in the form of  $Ag(NH_3)_2Cl$ , which, on acidification with  $HNO_3$ , will yield a white precipitate of  $AgCl$ .

While ammonium hydroxide dissolves  $AgCl$ , it offers at the same time an indication of the presence or absence of Hg; for the latter in the form of chloride is blackened by the reagent. To confirm the presence of Hg, the black residue is taken into solution with *aqua regia*, whereby it is converted into  $HgCl_2$ , and the latter is then tested for with  $SnCl_4$ . A white precipitate of  $HgCl$  or a gray precipitate of mercury (see this reaction under Hg) proves the presence of Hg in the original solution.

## SCHEME I

To the clear original solution contained in a *small beaker*, add dilute HCl drop by drop with constant stirring until no further precipitation takes place (1)\*; add 2 cc. more in excess and filter. If no precipitate forms, the absence of Ag, Hg (-ous), and large amounts of Pb (2) is indicated; in that case treat the solution with H<sub>2</sub>S in accordance with directions given on page 62.

The filtrate should be caught in a beaker of at least 150 cc. capacity, labeled Groups II.-V., and reserved. The precipitate is first washed with 2 cc. of dilute HCl (3), and finally with a stream of cold water from a wash bottle. Reject the washings. The precipitate may contain PbCl<sub>2</sub>, AgCl, and HgCl.

Pour through the filter holding the precipitate several small portions of hot water, using about 2 cc. at a time and allowing each portion to drain before adding the next. Divide the aqueous extract into two equal portions, and test it for Pb by adding to the first portion dilute H<sub>2</sub>SO<sub>4</sub>—a white precipitate is PbSO<sub>4</sub>; to the second portion add K<sub>2</sub>CrO<sub>4</sub>—a yellow precipitate is PbCrO<sub>4</sub> and confirms the presence of Pb. If no precipitates are obtained, Pb is absent from Group I.

Repeatedly wash the precipitate on the filter paper with hot water until the washings no longer react with dilute H<sub>2</sub>SO<sub>4</sub>. The residue on the filter may now consist of AgCl and HgCl. Pour a few drops of ammonium hydroxide on the filter and catch the liquid passing through in a test tube. Repeat until about 15–20 drops have been used. A blackening of the residue on the filter indicates the presence of Hg. The ammoniacal extract, if not clear (4), should be passed again through the same filter and tested for Ag by acidifying with HNO<sub>3</sub> (5). A white precipitate or cloudiness proves the presence of silver (6).

To confirm the presence of Hg, remove (7) as much as possible of the black precipitate remaining on the filter to a small evaporating dish, add 1–2 cc. of *aqua regia* (8) (15 drops of concentrated HCl to 5 drops of concentrated HNO<sub>3</sub>), and heat under the hood on wire gauze until dissolved; boil to destroy the excess of *aqua regia* (9), dilute with 1 cc. of water, filter (10).

\* The numbers in brackets refer to notes.

if necessary, and test the *clear* solution for Hg by adding a few drops of  $\text{SbCl}_3$ . A white precipitate, which may turn gray to black, confirms the presence of Hg.

#### NOTES

1. A white precipitate, when dilute HCl is used, may be due to  $\text{SbOCl}$  or  $\text{BiOCl}$ ; the latter, however, dissolves in excess of HCl.

To insure complete precipitation, HCl must be added in slight excess; this point is best ascertained by filtering a small portion of the mixture, and adding to the clear filtrate a drop or two of HCl, when, if the precipitation was complete, no further precipitate will be obtained; if a precipitate does form, more HCl must be added to the original solution until the test shows complete precipitation. A large excess of HCl is to be avoided on account of the appreciable solubility of the chlorides in an excess.

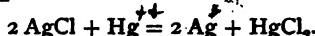
2.  $\text{PbCl}_3$  is somewhat soluble in cold  $\text{H}_2\text{O}$ , and while the presence of HCl diminishes its solubility, a small amount always remains unprecipitated by HCl and passes into the filtrate, from which it is precipitated by  $\text{H}_2\text{S}$  in Group II. One must therefore always look for Pb in the second group.

3. The precipitate is washed first with HCl, instead of  $\text{H}_2\text{O}$ , to prevent the formation of the oxychlorides of Bi and Sb. It is then washed with  $\text{H}_2\text{O}$  to remove the HCl, which would interfere with the solution of  $\text{PbCl}_2$  in hot water.

4. If all the Pb has not been extracted, it will be changed by ammonia to the insoluble basic compound  $\text{Pb}(\text{OH})\text{Cl}$ , which frequently passes through the filter. As this precipitate is soluble in  $\text{HNO}_3$ , it does not interfere with the test for Ag.

5. In acidifying a solution, it is imperative thoroughly to mix the solution after the addition of the acid, and then to test it with litmus. A solution in a test tube can be mixed by placing the thumb over the mouth of the tube and shaking. If the solution is contained in a beaker, thorough mixing is effected by stirring with a glass rod.

6. A cloudiness or turbidity is as conclusive a reaction as the formation of a large precipitate, provided the precaution is taken to see that both the solution to be tested and the reagent are perfectly clear. It is important to remember that when the amount of Hg is large and that of silver relatively small, ammonium hydroxide may fail to extract any  $\text{AgCl}$ , owing to the fact that the latter is reduced by the mercury of the black mixture ( $\text{NH}_4\text{HgCl} + \text{Hg}$ ) to the metallic state:—



When, therefore, a large black residue is obtained with ammonium hydroxide, and the test for Ag is negative, it becomes necessary to recover any Ag—the black mixture may contain after the treatment with *aqua regia* as described in note 10.

7. When the precipitate is large, a small amount may be removed with a glass or horn spatula. If too small to be handled in this way, recourse may be had to one of the following methods: (a) The funnel containing the filter is held horizontally with its rim resting against the edge of an evaporating dish or beaker, and the precipitate is washed out by directing a forceful stream of water from a wash bottle against the filter, at the same time giving the funnel a rotary motion. (b) By carefully perforating the apex of the filter with a platinum wire and gradually enlarging the hole (in this way clogging of the stem with filter paper is avoided); the precipitate can then be readily washed out with a forceful stream of water from a wash bottle. In this case, as in (a), the water should be carefully decanted after the precipitate has settled and then the precipitate should be treated with the solvent directed to be used. (c) Where the amount is very small and firmly adheres to the filter, it can be gotten into solution by the following procedure: Remove the filter from the funnel, close it up, and dry it by pressing it between the folds of several thicknesses of filter paper; then unfold it, tear away portions to which no precipitate adheres, and spread the rest of the paper with the precipitate uppermost on the bottom of an evaporating dish. Pour the solvent on the filter paper, heat, and stir with a glass rod till solution takes place; dilute with a little water and filter off the paper.

8. *Aqua regia* should always be prepared in small amounts immediately before use, and the cold mixture brought in contact with the substance to be dissolved and then heated. In contact with a substance it is capable of dissolving, it acts like Cl, and as the latter is an oxidizing agent, the chloride formed will be that of the highest valence of the metal capable of existing under the conditions.

9. Prolonged boiling has the effect of destroying *aqua regia* in accordance with the equation



The excess must be destroyed because its presence would oxidize the  $\text{SnCl}_2$  to  $\text{SnCl}_4$ . As the latter does not react with  $\text{HgCl}_2$ , the test would be worthless.

10. The solution is diluted because of the possible presence of  $\text{AgCl}$ , which is appreciably soluble in strong HCl. The residue, after filtration, is tested for Ag by first thoroughly washing it with  $\text{H}_2\text{O}$ , dissolving it in ammonium hydroxide, and reprecipitating by acidification with  $\text{HNO}_3$ .

### Reactions of Metals of Group II. Division A

#### MERCURY IN MERCURIC SALTS

Most of the salts of mercury are colorless and poisonous. The aqueous solutions of the normal salts have an acid reaction due to hydrolysis; they all volatilize on ignition.

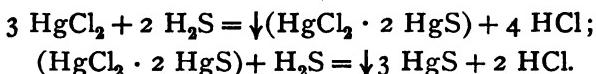
**1. Potassium or Sodium Hydroxide** gives a precipitate which at first is brownish but rapidly changes on further addition of the reagent to yellow HgO, insoluble in excess :—



**2. Ammonium Hydroxide** produces in solutions of the mercuric chloride a white precipitate of mercuric amido-chloride ; from solutions of the nitrate, a white precipitate of mercuric amido-nitrate :—

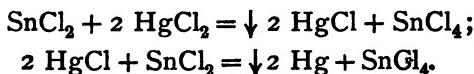


**3. Hydrogen Sulphide**, on being passed slowly into a solution of  $\text{HgCl}_2$ , forms at first a white precipitate which changes on further treatment with  $\text{H}_2\text{S}$  to a yellow, then brown, and finally to a black precipitate of  $\text{HgS}$ . These light-colored precipitates are mixtures of  $\text{HgCl}_2$  and  $\text{HgS}$  in varying proportions ; they are soluble in  $\text{HNO}_3$ , and are converted by further treatment with  $\text{H}_2\text{S}$  or with  $(\text{NH}_4)_2\text{S}$  to black  $\text{HgS}$  :—



$\text{HgS}$  is insoluble in dilute  $\text{HCl}$  ; also in hot dilute  $\text{HNO}_3$  (difference from the sulphides of Pb, Bi, Cu, and Cd). Prolonged boiling with strong  $\text{HNO}_3$  converts it into the white compound  $2 \text{ HgS} \cdot \text{Hg}(\text{NO}_3)_2$ , which is quite insoluble in dilute  $\text{HNO}_3$ .  $\text{HgS}$  is soluble in *aqua regia* with the formation of  $\text{HgCl}_2$  and the separation of sulphur ; it is practically insoluble in  $(\text{NH}_4)_2\text{S}$ , but completely soluble in  $\text{Na}_2\text{S}$  in the presence of sodium hydroxide.

**4. Stannous Chloride**, added in small quantity to a solution of  $\text{HgCl}_2$ , precipitates white  $\text{HgCl}$ , which is reduced by an excess of the reagent to black metallic  $\text{Hg}$  :—



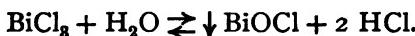
**5. Metallic Cu, Zn, or Fe**, when introduced into a solution of a mercuric salt, acidified, precipitates metallic  $\text{Hg}$ .

6. Potassium Iodide yields a red precipitate of  $\text{HgI}_2$ , soluble in excess of the reagent or the mercury salt.

7. If a dry mixture or a mercuric salt and  $\text{Na}_2\text{CO}_3$  is heated in an ignition tube, a sublimate of metallic Hg will be formed in the upper portion of the tube.

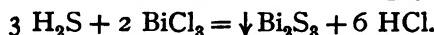
### BISMUTH

Nearly all the bismuth salts are white or colorless. The aqueous solutions always have an acid reaction, and if the dilution is large, the salt is decomposed with the formation of an insoluble basic salt; e.g.—

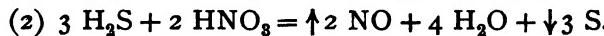
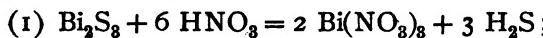


This reaction is very characteristic of bismuth salts and is interfered with by the presence of much acid. Because of their tendency to hydrolyze with water, aqueous solutions of bismuth salts can only be prepared with the aid of an acid.

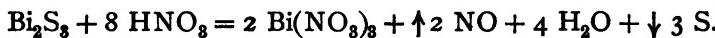
1. Hydrogen Sulphide precipitates black  $\text{Bi}_2\text{S}_3$ :—



The precipitate is insoluble in cold dilute acids, but dissolves in boiling dilute  $\text{HNO}_3$ :—



Adding (1) and (2), and eliminating 3  $\text{H}_2\text{S}$ , we get



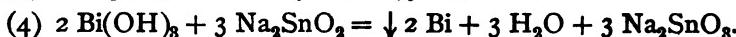
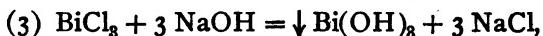
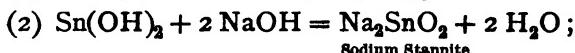
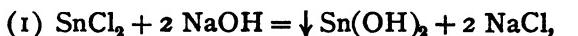
Bismuth sulphide is insoluble in  $(\text{NH}_4)_2\text{S}_x$ .

2. Potassium, Sodium, or Ammonium Hydroxide precipitates white  $\text{Bi}(\text{OH})_3$ , insoluble in excess. Its insolubility in excess of  $\text{NH}_4\text{OH}$  distinguishes it from Cu and Cd; the precipitate is soluble in dilute acids, however.

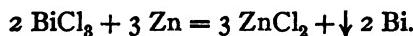
3. Water, when added in large amount to Bi salts, precipitates white basic salts; the chloride gives  $\downarrow \text{BiOCl}$ , the nitrate  $\downarrow \text{BiONO}_3$ , and the sulphate  $\downarrow (\text{BiO})_2\text{SO}_4$ . These are all soluble in dilute inorganic acids and are changed by  $\text{H}_2\text{S}$  to  $\text{Bi}_2\text{S}_3$ :—



4. Sodium Stannite in alkaline solution (prepared by adding NaOH to  $\text{SnCl}_4$  till the precipitate which first forms dissolves) gives with bismuth solutions a black precipitate of metallic bismuth :—



5. Metallic Zn or Fe, when added to a solution of a Bi salt, precipitates metallic Bi :—



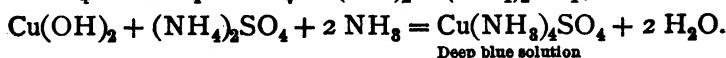
### COPPER

Copper forms two classes of salts; viz., the cuprous compounds, in which Cu is monovalent; and the cupric compounds, in which Cu is divalent. The former are very unstable, being readily oxidized to the cupric compounds; they are insoluble in water, but are soluble in halogen acids with the formation of colorless solutions. The cupric salts, when dissolved in water, yield blue or green solutions which have an acid reaction.

### REACTIONS OF THE CUPRIC SALTS

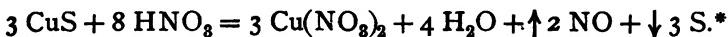
1. Sodium or Potassium Hydroxide precipitates light blue  $\text{Cu}(\text{OH})_2$ , soluble in a *large* excess of the strong reagent with the formation of a blue liquid. The precipitate is changed on boiling to black CuO. In the presence of sufficient tartaric, citric, or arsenic acid, NaOH fails to precipitate Cu salts.

2. Ammonium Hydroxide, largely diluted and added *cautiously* to solutions of copper salts, precipitates a light blue basic salt, readily soluble in excess, producing a deep blue solution, due to the formation of a cupric ammonia salt :—



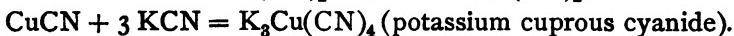
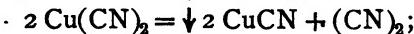
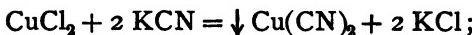
When  $\text{CuCl}_2$  is used, the blue compound formed with an excess of  $\text{NH}_3$  is  $\text{Cu}(\text{NH}_3)_4\text{Cl}_2$ . The sensitiveness of the test is 1 part in 25,000; it therefore is an exceedingly good test except for traces of the metal.

**3. Hydrogen Sulphide** produces in Cu solutions a black precipitate of  $\text{CuS}$  which is insoluble in dilute acids and alkalies, insoluble in sodium sulphide, but somewhat soluble in ammonium sulphide, especially if the latter is yellow and hot; it is insoluble in hot dilute  $\text{H}_2\text{SO}_4$  (distinction from Cd). When freshly precipitated,  $\text{CuS}$  is easily soluble in  $\text{KCN}$  solution; it is also soluble in hot dilute  $\text{HNO}_3$  with the separation of S:—

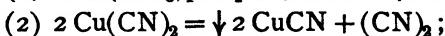
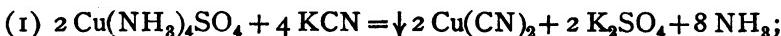


When exposed to the air in moist condition,  $\text{CuS}$  oxidizes to  $\text{CuSO}_4$ .

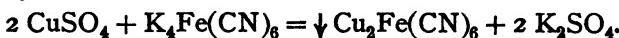
**4. Potassium Cyanide** produces a yellow precipitate of  $\text{Cu}(\text{CN})_2$ , which immediately decomposes into white cuprous cyanide ( $\text{CuCN}$ ) and cyanogen; on adding an excess of the reagent, the precipitate dissolves, with the formation of a complex cyanide of K and Cu:—



From solutions of  $\text{K}_3\text{Cu}(\text{CN})_4$ ,  $\text{H}_2\text{S}$  does not precipitate  $\text{CuS}$  (distinction from Cd). If to the deep blue solution of  $\text{Cu}(\text{NH}_3)_4\text{SO}_4$  potassium cyanide is added, the color will be bleached, due to the formation of  $\text{K}_3\text{Cu}(\text{CN})_4$ :—



**5. Potassium Ferrocyanide** precipitates reddish brown cupric ferrocyanide:—



\* Resolvable into 2 steps (see PbS).

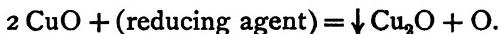
It is insoluble in dilute acids, but soluble in NH<sub>4</sub>OH with the formation of a blue solution. The reaction with K<sub>4</sub>Fe(CN)<sub>6</sub> is by far the most sensitive test for Cu; with very dilute solutions, it gives a reddish brown coloration. The sensitiveness of the tests is 1 part in 200,000.

6. Potassium Iodide yields with solutions of cupric salts a yellowish white precipitate of cuprous iodide (Cu<sub>2</sub>I<sub>2</sub>); at the same time iodine is liberated and turns the solution brown:—



7.  $\alpha$  Amino Normal Caproic Acid.\* An aqueous solution of this compound when added to a solution of copper not too strongly acid yields a characteristic crystalline precipitate of copper  $\alpha$  normal amino caproate. This is one of the most sensitive tests for copper and is capable of detecting 0.004 mg. of copper with certainty.

8. Certain organic substances, like glucose, reduce copper solutions with the precipitation of red Cu<sub>2</sub>O. The test is best carried out by adding to the copper solution KNaC<sub>4</sub>H<sub>4</sub>O<sub>6</sub> (Rochelle salt) and NaOH, the latter being added until the resulting solution assumes a deep blue color. On boiling and adding a small quantity of glucose, a red precipitate of Cu<sub>2</sub>O is obtained. The reaction consists essentially of



9. Many metals reduce solutions of Cu salts to the metallic state; e.g., Zn, Cd, Al, Fe. If an iron nail is immersed in a solution containing a Cu salt slightly acidified with HCl, a bright deposit of metallic Cu is formed on the iron. As dilute a solution as 1 part in 120,000 of water will give this test.

Cu salts, when ignited in the bunsen flame, impart to it a green color which is intensified if the Cu solution contains HCl.

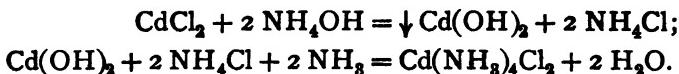
### CADMIUM

The cadmium salts are for the most part colorless. The nitrate, chloride, sulphate, bromide, iodide, and acetate are soluble in water.

\* Lyle, Curtman and Marshall, J. A. C. S., 37, (1915), 1471.

1. Potassium or Sodium Hydroxide precipitates white  $\text{Cd}(\text{OH})_2$ , insoluble in excess.

2. Ammonium Hydroxide precipitates white  $\text{Cd}(\text{OH})_2$ , soluble in excess, forming complex ammonia salts:—

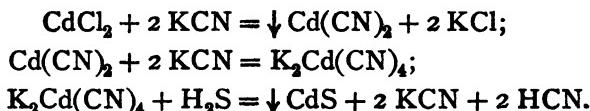


This ammonia salt, like the corresponding Cu salt, may be transposed to the double cyanide,  $\text{K}_2\text{Cd}(\text{CN})_4$ , by a KCN solution.

3. Hydrogen Sulphide precipitates, from solutions not too strongly acid, yellow  $\text{CdS}$ , insoluble in cold dilute acids, alkali hydroxides, and  $(\text{NH}_4)_2\text{S}$ ; and insoluble in KCN (distinction from Cu). It is soluble in hot dilute  $\text{HNO}_3$  with the separation of S (reaction similar to Pb, which see), and soluble in hot dilute  $\text{H}_2\text{SO}_4$  (difference from Cu).

From hot slightly acidulated solutions,  $\text{H}_2\text{S}$  precipitates red  $\text{CdS}$ .

4. Potassium Cyanide yields a white precipitate,  $\text{Cd}(\text{CN})_2$ , soluble in excess, with the formation of  $\text{K}_2\text{Cd}(\text{CN})_4$ , from which  $\text{H}_2\text{S}$  precipitates  $\text{CdS}$  (distinction from Cu):—



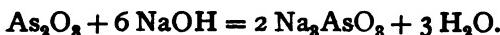
### Reactions of the Metals of Group II. Division B

#### ARSENIC

Arsenic forms two series of compounds. Those in which it plays the rôle of a trivalent metal are known as the *arsenious* compounds; and those in which the metal is pentavalent are known as the *arsenic* compounds. The two oxides  $\text{As}_2\text{O}_3$  and  $\text{As}_2\text{O}_5$  are respectively the anhydrides of arsenious ( $\text{H}_3\text{AsO}_3$ ) and arsenic ( $\text{H}_3\text{AsO}_4$ ) acids.

### *Reactions of the Arsenious Compounds*

The arsenious compounds may be considered as derived from  $\text{As}_2\text{O}_3$ . The latter, on treatment with boiling water, yields  $\text{H}_3\text{AsO}_3$ ; the oxide also dissolves in alkalies with the formation of soluble alkali arsenites. All other arsenites are insoluble in water.

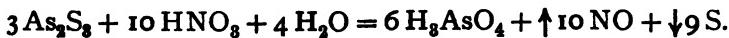


1.  $\text{NaOH}$ ,  $\text{NH}_4\text{OH}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{HCl}$ , and  $\text{H}_2\text{SO}_4$  do not precipitate As from its compounds.

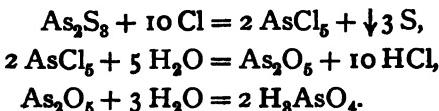
2. **Hydrogen Sulphide.** From neutral solutions of arsenites or from aqueous solutions of  $\text{As}_2\text{O}_3$ ,  $\text{H}_2\text{S}$  does not precipitate the sulphide but colors the solution yellow, which is due to the formation of colloidal  $\text{As}_2\text{S}_3$ : if, however, the solution is acidified with  $\text{HCl}$ , a yellow precipitate of  $\text{As}_2\text{S}_3$  immediately forms:—



The precipitate is insoluble in concentrated  $\text{HCl}$  (distinction from Sb and Sn), hence the presence of a large quantity of free acid does not interfere with the precipitation with  $\text{H}_2\text{S}$ . Concentrated  $\text{HNO}_3$ , *aqua regia*, or a mixture of concentrated  $\text{HCl}$  and  $\text{KClO}_3$  readily oxidizes  $\text{As}_2\text{S}_3$  to arsenic acid ( $\text{H}_3\text{AsO}_4$ —soluble in water) with the separation of S. Ammonium sulphide and alkali hydroxides both dissolve  $\text{As}_2\text{S}_3$  (distinction from the sulphides of Division A).



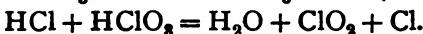
The action of *aqua regia* on  $\text{As}_2\text{S}_3$  may be represented by the following equations:—



Adding these 3 equations, with the elimination of substances appearing on both sides, we get as the final result:—



The action of  $\text{KClO}_3 + \text{HCl}$  may be represented thus :—

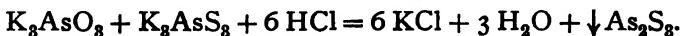


It is evident that this mixture behaves somewhat like *aqua regia*.

The deportment of KOH is as follows :—



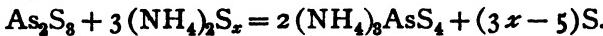
$\text{K}_3\text{AsS}_3$  may be regarded as derived from potassium arsenite ( $\text{K}_3\text{AsO}_3$ ), by replacement of the oxygen by S; hence it is called potassium thioarsenite. If this mixture of thioarsenite and arsenite is acidified with HCl,  $\text{As}_2\text{S}_3$  is reprecipitated :—



The equation for the solution of  $\text{As}_2\text{S}_3$  in  $(\text{NH}_4)_2\text{S}$  is —



If  $(\text{NH}_4)_2\text{S}_x$  is used, we get ammonium thioarsenate :—



The excess of S in the polysulphide oxidizes the thioarsenite to thioarsenate. The  $(3x - 5)\text{S}$  does not separate out but dissolves in the excess of  $(\text{NH}_4)_2\text{S}_x$  to form a higher polysulphide.

If the solution of  $\text{As}_2\text{S}_3$  in  $(\text{NH}_4)_2\text{S}_x$  is acidified with HCl, the As is reprecipitated as yellow  $\text{As}_2\text{S}_5$  :—



but as this solution always contains an excess of  $(\text{NH}_4)_2\text{S}_x$ , the following reaction will also take place simultaneously :—



3. Silver Nitrate precipitates from neutral solutions of arsenites yellow silver arsenite,  $\text{Ag}_3\text{AsO}_3$  (distinction from arsenates) :—



The precipitate is easily soluble in acids and alkalies.

4. Magnesium mixture (solution of  $\text{MgCl}_2 + \text{NH}_4\text{Cl} + \text{NH}_3$ ) does not precipitate arsenites (difference from arsenates).

5. Iodine in solutions rendered alkaline with  $\text{NaHCO}_3$  readily oxidizes arsenites to arsenates :—

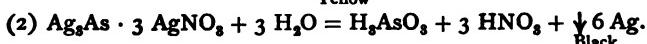


### Special Tests for the Detection of Minute Amounts of Arsenic

1. The so-called **Marsh Test** for arsenic and its modifications is based on the fact that when arsenic compounds are introduced into a hydrogen generator ( $Zn + H_2SO_4$ ), the As compound is reduced to gaseous arsine ( $AsH_3$ ), which escapes along with the excess of hydrogen. If the dried gases are led into a hard glass tube heated to redness, the arsine will be decomposed and a deposit of metallic arsenic will form in the tube just beyond the part heated. If the gases are ignited, they burn with a bluish white flame; if a piece of cold porcelain is held in this flame, it will receive a black coating which is readily soluble in a solution of sodium hypobromite ( $NaBrO$ ) (distinction from Sb). In making this test, it is necessary to run what is called a *blank* to make sure that the apparatus and the reagents employed in the test are arsenic-free. This is accomplished by carrying out the test precisely as described, except that no arsenic compound is added; and if the materials are arsenic-free, no mirror will be formed. Unless the results of this test are controlled by a blank, it cannot be considered trustworthy, for ordinary pure zinc and sulphuric acid, as well as glass tubing, usually contain sufficient arsenic to yield a positive result.

For the detection of arsenic in wall paper as well as in reagents, medicinal preparations, and foods, the following tests are employed. The first two are modifications of the Marsh test; but all have the advantage over the Marsh test in that they are more rapid and require no special apparatus.

2. The **Gutzeit Test** for arsenic depends upon the fact that arsine colors a solution of silver nitrate (1:1) first yellow and finally black. To carry out this test, put in a test tube a few pieces of arsenic-free zinc and cover with about 3 cc. of dilute sulphuric acid. Place near the top of the tube a plug of cotton, stopper the tube with a loosely fitting cork which has been covered with 2 folds of filter paper moistened with  $AgNO_3$  solution (1:1), and allow to stand several minutes. If no darkening of the paper is produced, the blank is satisfactory. Now remove the plug and stopper, and introduce a very small amount of the solution or substance to be tested for arsenic. Replace the plug and stopper, and allow to stand again for several minutes. A yellow stain which quickly becomes black proves the presence of arsenic. Frequently, especially with solutions of silver nitrate less concentrated than 1:1, the yellow stage is not seen. The reactions involved are the following:—

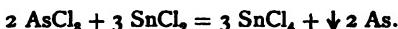


Phosphine, stibine, and hydrogen sulphide interfere with this reaction; the last can be guarded against by moistening the cotton plug with lead acetate solution. Instead of  $AgNO_3$ ,  $HgCl_2$  may be used; this yields a yellow stain.

3. **Fleitmann Test.** As the Gutzeit test does not distinguish between arsenic and antimony, Fleitmann devised a method by which the arsenic alone can be detected. This consists in generating the arsine in an alkaline solution.

**METHOD.** Into a test tube place a small piece of arsenic-free Zn or Al; cover with a few cubic centimeters of NaOH and heat to boiling to start the reaction, then remove from flame, add the arsenic solution, cap with stopper covered with paper moistened with silver nitrate solution, and allow to stand; a blackening proves the presence of arsenic. If the arsenic is in the pentad state, it should first be reduced with SO<sub>2</sub> before applying this test.

4. **Bettendorff's Test** depends upon the fact that in a solution strongly acid with hydrochloric acid, stannous chloride reduces arsenic compounds to metallic arsenic: —



The test is carried out as follows: To 2 cc. of concentrated HCl in a test tube, add 1 cc. of strong SnCl<sub>2</sub> solution; then add a few drops of the solution to be tested for As and heat gently. A brown color or precipitate indicates the presence of arsenic. Antimony is not reduced under these conditions. The addition of a small piece of tin foil will have the effect of hastening the reaction, but must not be used if bismuth or antimony is known to be present.

5. **Reinsch Test.** If a solution containing arsenic, to which  $\frac{1}{2}$  of its bulk of concentrated HCl has been added, is boiled with a strip of bright copper foil, the latter becomes coated with a gray deposit of copper arsenide (Cu<sub>3</sub>As<sub>2</sub>). If the foil is removed, washed, and dried between the folds of filter paper, and then slowly and carefully heated in a dry test tube, a white crystalline sublimate of As<sub>2</sub>O<sub>3</sub> will form; the latter can readily be recognized by examining with a lens or confirmed by dissolving in boiling water and applying the Fleitmann test.

#### Sensitiveness of the Special Arsenic Tests

Marsh test will detect 1 part of As in	200,000,000;
Gutzzeit test will detect 1 part of As in	10,000,000;
Bettendorff test will detect 1 part of As in	7,000,000; and
Reinsch test will detect 1 part of As in	40,000.

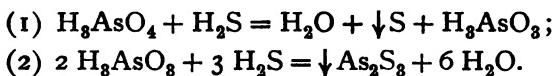
Any solid substance containing arsenic, when mixed intimately with four times its weight of a mixture of KCN and Na<sub>2</sub>CO<sub>3</sub>, and heated in an ignition tube, will yield a black mirror of metallic arsenic on the cooler part of the tube. The sensitiveness of this test is 1 part in 8000.

**Oxidation** of arsenious to arsenic compounds can be accomplished by the addition of iodine; the reaction proceeds best in a solution alkaline with sodium dicarbonate: —

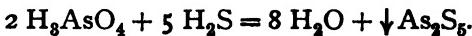


*Reactions of Arsenic Compounds*

1. NaOH, KOH, NH<sub>4</sub>OH or Na<sub>2</sub>CO<sub>3</sub> produces no precipitate.
2. Hydrogen Sulphide. From cold, moderately acid solutions of arsenic acid, H<sub>2</sub>S precipitates, after some time, a mixture of As<sub>2</sub>S<sub>3</sub> + S. The H<sub>2</sub>S first reduces the arsenic acid with the separation of sulphur, and then precipitates As<sub>2</sub>S<sub>3</sub> readily from the reduced arsenic (-ic) solution :—



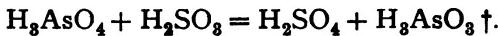
If the arsenic solution is heated, the reduction and precipitation are hastened. If the amount of HCl is considerable, the stream of H<sub>2</sub>S rapid, and the solution cold, all of the As will be precipitated as As<sub>2</sub>S<sub>5</sub> :—



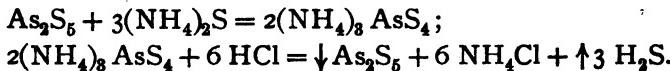
When, under the same conditions of acidity, the solution is heated and then treated with a rapid stream of H<sub>2</sub>S, a mixture of As<sub>2</sub>S<sub>3</sub> and As<sub>2</sub>S<sub>5</sub> is obtained.

To rapidly precipitate the arsenic existing in the pentad state, it should be first reduced by adding sulphurous acid (H<sub>2</sub>SO<sub>3</sub>) to the cold solution and boiling till the excess of SO<sub>2</sub> is expelled.\*

From the resulting reduced solution, H<sub>2</sub>S will rapidly precipitate the arsenic as As<sub>2</sub>S<sub>3</sub> :—



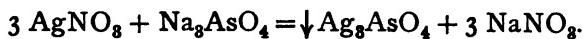
As<sub>2</sub>S<sub>5</sub> has the same solubility as As<sub>2</sub>S<sub>3</sub>; it dissolves in (NH<sub>4</sub>)<sub>2</sub>S with the formation of ammonium thioarsenate, from which HCl reprecipitates As<sub>2</sub>S<sub>5</sub> :—



\* The reduction is best accomplished by adding the H<sub>2</sub>SO<sub>3</sub> to the cold solution contained in a pressure bottle, stoppering, and heating in a boiling water bath for one hour. The bottle should be thoroughly cooled before opening.

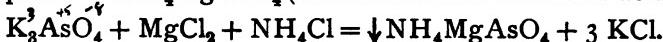
† If alkaline earth metals are present, they will be precipitated by the H<sub>2</sub>SO<sub>4</sub> formed.

3. **Silver Nitrate** precipitates from strictly neutral solutions chocolate-colored  $\text{Ag}_3\text{AsO}_4$  (distinction from arsenious and phosphoric acids):—



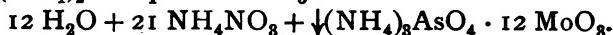
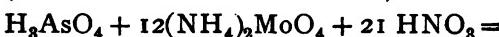
The precipitate is easily soluble in acids and in ammonium hydroxide.

4. **Magnesia mixture** yields (better when the solutions are cold) with neutral or ammoniacal solutions a white crystalline precipitate of  $\text{NH}_4\text{MgAsO}_4$  (distinction from arsenious acid):—



The precipitate is soluble in acids, but insoluble in 2.5 per cent ammonia water.

5. **Ammonium Molybdate**, when added in great excess to a hot nitric acid solution of arsenic acid, yields a yellow precipitate of ammonium arsenomolybdate of variable composition (distinction from arsenious acid):—



The presence of  $\text{NH}_4\text{NO}_3$  favors this reaction. The precipitate is soluble in ammonium hydroxide, also in an excess of  $\text{H}_3\text{AsO}_4$ ; hence the necessity of having an excess of the reagent. Phosphates, or phosphoric acid, give a precipitate of similar appearance, hence they should be absent in making the test.

6. **Reducing Agents**, like  $\text{FeSO}_4$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{Na}_2\text{SO}_3$ , when boiled with a solution of an arsenate strongly acid with HCl, reduce the substance from the arsenic to the arsenious state.

Any arsenic compound, when treated with strong HCl and distilled in a current of HCl gas, will yield a distillate of  $\text{AsCl}_3$ .

**Potassium Iodide**, when added to an acid solution of  $\text{H}_3\text{AsO}_4$ , will reduce it to  $\text{H}_3\text{AsO}_3$  with the separation of iodine:—



This test serves to detect arsenic acid in the presence of arsenious acid.

**Special Tests for the Detection of Small Amounts.** In the Marsh and Gutzeit tests, the reduction to  $\text{AsH}_3$  takes place less

rapidly, due to the necessity of a preliminary reduction of  $H_3AsO_4$  to  $H_3AsO_3$ :—



With the Fleitmann test, preliminary reduction with  $H_2SO_3$  is necessary.

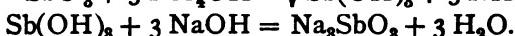
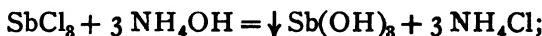
### ANTIMONY

Like arsenic, antimony forms two series of compounds, viz., antimonic salts, in which antimony acts as pentavalent; and antimonious compounds, in which antimony behaves as a trivalent element.

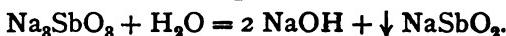
#### *Reactions of Antimonious Compounds*

In carrying out the following reactions a hydrochloric acid solution of  $SbCl_3$  may be employed.

i. **Sodium Hydroxide, Ammonium Hydroxide, and Sodium Carbonate** each precipitates white antimonious hydroxide,  $Sb(OH)_3$ , insoluble in ammonium hydroxide, but soluble in an excess of the fixed caustic alkalies and in a hot solution of alkali carbonate:—



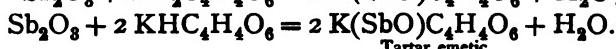
$Na_3SbO_3$  readily hydrolyzes in contact with water, yielding sodium metantimonite,  $NaSbO_2$ :—



The latter is further hydrolyzed by water, yielding finally white  $Sb_2O_3$ :—  $2 NaSbO_2 + H_2O = 2 NaOH + \downarrow Sb_2O_3$ .

$Sb_2O_3$  is practically insoluble in water and in nitric acid, but readily dissolves in hot concentrated HCl with the formation of  $SbCl_3$ .

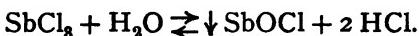
Tartaric acid and the tartrates dissolve it in accordance with the following equations:—



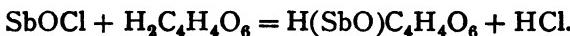
In both of the resulting soluble compounds of antimony, the group ( $SbO$ ), called antimonyl, acts as a monovalent radical similar to ( $NO$ ), nitrosyl, in nitrosyl sulphuric acid,  $H(NO)SO_4$ ;

tartar emetic may, therefore, be called potassium antimonyl tartrate. The solubility of antimony compounds in tartaric acid is of great analytical importance.

**2. Water.** If to a solution of  $SbCl_3$  containing not too much free acid a relatively large quantity of water is added, there forms a white precipitate of antimony oxychloride,  $SbOCl$ :—



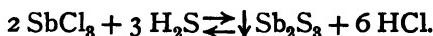
As indicated, the reaction is reversible, too much HCl having the effect of reversing the reaction; precipitation may be hastened by heating. The precipitate is easily distinguished from the corresponding bismuth compound by its solubility in tartaric acid:—



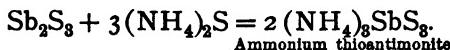
The precipitate is also soluble in strong HCl and can be changed directly to  $Sb_2S_3$  by  $H_2S$ :—



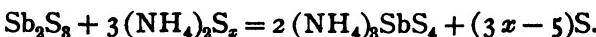
**3. Hydrogen Sulphide.** From solutions not too strongly acid with HCl,  $H_2S$  precipitates red  $Sb_2S_3$ :—



The reversibility of the reaction indicates that a high concentration of HCl would prevent the precipitation, also that the precipitate when formed would dissolve in strong HCl. It has been found by experiment that HCl (1:1) readily dissolves  $Sb_2S_3$  (distinction and method of separation from As).  $Sb_2S_3$  is soluble in  $(NH_4)_2S$  with the formation of a thio salt:—

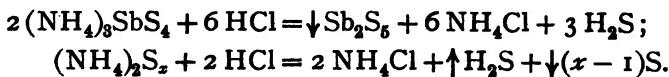


If yellow  $(NH_4)_2S$  is used, the excess of sulphur in the latter oxidizes the thioantimonite formed in the last reaction to thioantimonate:—



The great similarity of the chemistry of the thio salts of antimony and arsenic is thus seen.

If the solution of  $Sb_2S_3$  in  $(NH_4)_2S_x$ —that is, the solution containing ammonium thioantimonate and an excess of  $(NH_4)_2S_x$ —is acidified with HCl, we get (as with the As compound) the higher sulphide precipitated and at the same time a separation of sulphur resulting from the decomposition of the excess of  $(NH_4)_2S_x$ :—



The sulphide of antimony is also soluble in alkalies, from solutions of which HCl reprecipitates  $Sb_2S_3$ .

**4. Zn-Pt Couple.** If a solution of antimony, acid with HCl, is poured into a dish containing a piece of platinum foil and a piece of zinc is added so that it touches the platinum, there will form on the platinum foil a black deposit or stain of metallic antimony. Even in dilute solutions this characteristic test can be applied. If arsenic is known to be present, the test should be carried out under a hood because of the possible formation of arsine.

**5.** If a solution of antimony, acid with HCl, is heated with a bright iron nail, all the antimony will be deposited in the form of black flocks (distinction from Sn).

#### *Antimonic Compounds*

**1. Water.** If a solution of  $SbCl_5$ , not too strongly acid with HCl, is diluted with a relatively large amount of water, a white precipitate of  $SbO_2Cl$  is formed:—

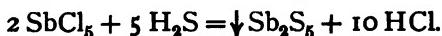


If the dilution is very great, the  $SbO_2Cl$  is further changed to antimonic acid:—



As with  $SbOCl$ , tartaric acid prevents the precipitation of  $SbO_2Cl$ .

**2. Hydrogen Sulphide.** From moderately acid solutions of  $\text{SbCl}_5$ ,  $\text{H}_2\text{S}$  precipitates orange-red  $\text{Sb}_2\text{S}_5$  :—



The precipitate is soluble in concentrated HCl with the formation of  $\text{SbCl}_3$  and evolution of  $\text{H}_2\text{S}$  :—



It possesses the same solubilities as the trisulphide, dissolving in  $(\text{NH}_4)_2\text{S}$  with the formation of ammonium thiantimonate,  $(\text{NH}_4)_3\text{SbS}_4$ ; on acidifying the latter with HCl, the pentasulphide is reprecipitated :—



$\text{Sb}_2\text{S}_5$  also dissolves in caustic alkalies.

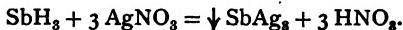
**3. Potassium Iodide,** when added to a HCl solution of  $\text{SbCl}_5$ , reduces it with the separation of iodine [distinction from Sb (-ous) compounds] :—



#### Special Tests for Small Amounts of Antimony

**1. The Marsh Test.** This is carried out in the same manner as directed for arsenic. The stibine ( $\text{SbH}_3$ ) which forms is decomposed in the hot tube with the separation of metallic antimony in the form of a black mirror which is insoluble in a solution of  $\text{NaBrO}$  (distinction from As).

$\text{SbH}_3$  is further distinguished from  $\text{AsH}_3$  by the formation of black  $\text{Ag}_3\text{Sb}$  when the former is passed into a solution of silver nitrate :—



With  $\text{AsH}_3$  the black deposit is due to metallic silver (see p. 49).

**2. Gutzeit Test.** Same as for As, the blackening being due to  $\text{Ag}_3\text{Sb}$ .

**3. The Reinsch Test,** when applied to antimony compounds, yields a black coating on the copper foil, which, when dried and ignited, gives a non-crystalline sublimate of  $\text{Sb}_2\text{O}_3$ . The latter is insoluble in water but is soluble in a hot solution of  $\text{KHC}_4\text{H}_4\text{O}_6$ , from which  $\text{H}_2\text{S}$  precipitates red  $\text{Sb}_2\text{S}_5$ .

Neither Fleitmann's nor Bettendorff's test are applicable to antimony compounds.

#### TIN

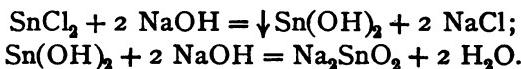
The two oxides of tin,  $\text{SnO}$  and  $\text{SnO}_2$ , correspond to two classes of salts known respectively as the *stannous* and *stannic*

compounds. In the former, tin is divalent; in the latter tetravalent.

### *Reactions of Stannous Salts*

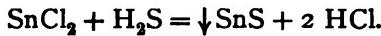
The stannous salts are all colorless. Those which are soluble in water yield solutions which have an acid reaction; the solid salts as well as their solutions rapidly absorb oxygen from the air with the formation of stannic compounds.

1. **Sodium Hydroxide, Ammonium Hydroxide, or Sodium Carbonate** gives a white precipitate of  $\text{Sn}(\text{OH})_2$ , which is readily soluble in excess of NaOH with the formation of sodium stannite; it is insoluble in excess of the other precipitants.

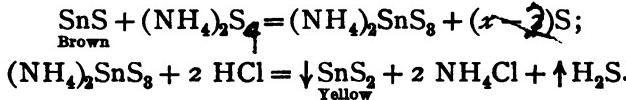


The precipitate also dissolves in HCl. It possesses, like  $\text{Al}(\text{OH})_3$ , both acid and basic properties; substances of this character are called *amphoteric* substances.

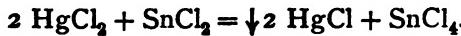
2. **Hydrogen Sulphide.** From moderately acid solutions (containing not more than 2.5 per cent. of concentrated HCl)  $\text{H}_2\text{S}$  throws down a brown precipitate of  $\text{SnS}$ :—



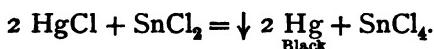
$\text{SnS}$  is soluble in strong HCl (distinction from As), nearly insoluble in colorless  $(\text{NH}_4)_2\text{S}$  [distinction from the sulphides of As, Sb, and Sn (-ic)], but is soluble in hot  $(\text{NH}_4)_2\text{S}_x$  with the formation of ammonium thiostannate, from which HCl precipitates yellow stannic sulphide,  $\text{SnS}_2$ :—



3. **Mercuric Chloride**, when added in excess to a solution of  $\text{SnCl}_2$ , is reduced to white insoluble  $\text{HgCl}$ ; the  $\text{SnCl}_2$  is oxidized at the same time to  $\text{SnCl}_4$ :—



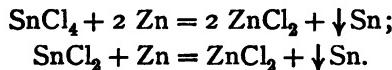
If, however, the  $\text{SnCl}_2$  is present in excess, the  $\text{HgCl}$  first formed is further reduced to metallic mercury (gray or black):—



As this reaction is essentially one of reduction, it is important that the  $\text{HgCl}_2$  solution contain no oxidizing agent. Stannic compounds do not give this reaction; it thus serves to distinguish stannous from stannic compounds.

4. **Bismuth salts** are reduced by an alkaline solution of stannous salts with the precipitation of black metallic bismuth (see under *Bismuth*, reaction 4).

5. **Metallic Zinc.** When metallic zinc is introduced into a hydrochloric acid solution of either  $\text{SnCl}_2$  or  $\text{SnCl}_4$ , metallic tin is precipitated on the zinc in the form of a gray spongy mass. As the deposited tin is readily soluble in strong  $\text{HCl}$ , care must be taken not to have the solution too strongly acid.



### *Stannic Compounds*

With the exception of the sulphide all the stannic compounds are either colorless or white. They are generally obtained from stannous salts by oxidation; thus, a solution of  $\text{SnCl}_4$  for the following tests may be prepared by warming a rather strong  $\text{HCl}$  solution of  $\text{SnCl}_2$ , with  $\text{KClO}_3$  added in small portions, until the solution becomes yellow, and then boiling off the excess of chlorine; after a slight dilution with water, the solution is ready for use.

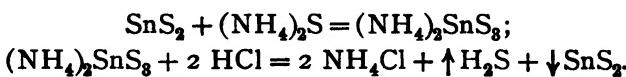
#### *Reactions of a Solution of $\text{SnCl}_4$*

1. **Sodium Hydroxide, Ammonium Hydroxide**, as well as **Sodium Carbonate**, yield a white precipitate of stannic hydroxide,  $\text{Sn}(\text{OH})_4$ , which, on drying, becomes  $\text{H}_2\text{SnO}_3$ . The precipitate is soluble in excess of  $\text{NaOH}$  or  $\text{Na}_2\text{CO}_3$  with the formation of sodium stannate of variable composition.

**2. Hydrogen Sulphide.** From moderately acid solutions not exceeding 2.5 per cent. concentrated HCl,  $H_2S$  precipitates yellow  $SnS_2$  :—



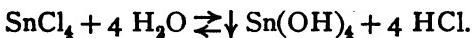
$SnS_2$  is readily soluble in HCl (1 : 1), hence the necessity for having the solution not too strongly acid. The disulphide of tin readily dissolves in colorless  $(NH_4)_2S$  (distinction from  $SnS$ ) with the formation of ammonium thiostannate, from which HCl precipitates  $SnS_2$  (yellow) :—



On strong ignition in the air,  $SnS_2$  is quantitatively converted into  $SnO_2$ .

**3. Mercuric Chloride** gives no precipitate with stannic salts (distinction from stannous).

**4.** Hydrochloric or sulphuric acid does not precipitate stannic salts from solutions that are moderately concentrated (distinction from metastannic compounds); when, however, the solutions are diluted and boiled, a precipitate of  $Sn(OH)_4$  is obtained :—

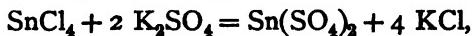


**5. Potassium or Sodium Sulphate.** From cold solutions no precipitate is obtained with these reagents (distinction from metastannic compounds); but, on boiling, a precipitate of  $Sn(OH)_4$  is obtained.

Reactions 4 and 5 can be explained on the assumption that the oxy-salts of stannic tin first form, but being unstable in dilute solutions are decomposed into stannic hydroxide, thus :—



Similarly, with  $K_2SO_4$  we get



the  $Sn(SO_4)_2$  being then hydrolyzed as shown above in equation (2).

### *Metastannic Compounds*

There are two forms of stannic compounds; viz., the normal and the metastannic forms. The normal may be considered as derived from stannic hydroxide, formed by the action of NaOH on  $\text{SnCl}_4$ . It is readily soluble in acids. The metastannic compounds are derived from metastannic acid, a white substance obtained by the action of hot dilute  $\text{HNO}_3$  on metallic tin; it has the same empirical formula as the partially dehydrated  $\text{Sn}(\text{OH})_4$ , i.e.,  $\text{H}_2\text{SnO}_5$ , but differs from it in being insoluble in acids. When boiled for a short time with concentrated HCl, a compound of the formula  $\text{Sn}_5\text{O}_5\text{Cl}_2(\text{OH})_8$  forms which, though quite insoluble in HCl, is readily soluble in water. From the fact that this and similar compounds may be formed from metastannic acid, the formula  $\text{Sn}_5\text{O}_5(\text{OH})_{10}$  or 5 ( $\text{H}_2\text{SnO}_5$ ) has been assigned to it. Stannic hydroxide, when dried over concentrated  $\text{H}_2\text{SO}_4$ , has the formula  $\text{H}_2\text{SnO}_5$ ; metastannic acid is thus seen to be a polymer of stannic hydroxide.

### *Reactions of Metastannic Chloride, $\text{Sn}_5\text{O}_5\text{Cl}_2(\text{OH})_8$*

1. HCl precipitates  $\text{Sn}_5\text{O}_5\text{Cl}_4(\text{OH})_6 \cdot 4 \text{H}_2\text{O}$ .
2. Prolonged boiling with water causes the precipitation of all the tin as metastannic acid, insoluble in dilute acids.
3.  $\text{H}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ , or  $\text{Na}_2\text{SO}_4$  precipitates a white substance which changes, on washing with water, to metastannic acid (distinction from stannic chloride).
4. KOH precipitates metastannic acid, which is converted by an excess of the concentrated reagent to a potassium salt; the latter is soluble in water and in dilute KOH solution.
5.  $\text{NH}_4\text{OH}$  precipitates metastannic acid.
6.  $\text{H}_2\text{S}$  yields the same precipitate as with  $\text{SnCl}_4$  solutions. Solutions of stannic compounds are converted into the metastannic form by diluting and boiling:—



Conversely, metastannic compounds are converted into the stannic form by boiling with concentrated HCl or concentrated KOH.

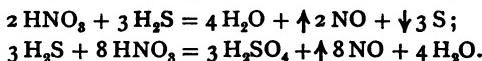
#### *Action of $\text{H}_2\text{S}$*

Besides its action as a group reagent for precipitating the metals of Group II.,  $\text{H}_2\text{S}$  also acts as a reducing agent. Should, therefore, an oxidizing agent be present in the solution subjected to the action of  $\text{H}_2\text{S}$ , it will be reduced, the  $\text{H}_2\text{S}$  being oxidized at the same time to elementary sulphur, which sepa-

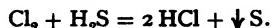
rates in a finely divided state, and, in some cases, partly to sulphuric acid. Among the oxidizing agents likely to be present in the filtrate from Group I. are  $\text{FeCl}_3$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{KMnO}_4$ ,  $\text{HNO}_3$ , and *aqua regia*. The reduction of the first three substances is accompanied by a change in color of the solution, thus frequently affording an indication of their presence. For example, a solution containing ferric salts undergoes a change from a yellow or reddish yellow to a colorless condition —  $2 \text{FeCl}_3 + \text{H}_2\text{S} = 2 \text{FeCl}_2 + 2 \text{HCl} + \downarrow \text{S}$ ; a  $\text{K}_2\text{Cr}_2\text{O}_7$  solution changes by the action of  $\text{H}_2\text{S}$  from reddish orange to green —  $\text{K}_2\text{Cr}_2\text{O}_7 + 3 \text{H}_2\text{S} + 8 \text{HCl} = 2 \text{CrCl}_3 + 2 \text{KCl} + 7 \text{H}_2\text{O} + \downarrow 3 \text{S}$ ; while a solution containing  $\text{KMnO}_4$  changes from a solution with purple tint to one that is colorless : —



Should the concentration of nitric acid be large, it will oxidize the  $\text{H}_2\text{S}$  with separation of sulphur and partly with the formation of  $\text{H}_2\text{SO}_4$  : —



*Aqua regia* will oxidize the  $\text{H}_2\text{S}$  in accordance with the equation —



It will be observed that in every case the presence of an oxidizing agent causes the decomposition of the  $\text{H}_2\text{S}$  with the separation of S; with a large amount of oxidizing agent present, the amount of S and  $\text{H}_2\text{SO}_4$  will be formed in quantity sufficient to seriously interfere with the analysis. A large quantity of sulphur is undesirable because it complicates and masks the results; and the presence of  $\text{H}_2\text{SO}_4$  will have the effect of precipitating the alkaline earths along with the metals of the second group, so that where the amount of oxidizing agent is large it is advisable to eliminate the latter before passing in  $\text{H}_2\text{S}$ . If, from the purple or orange-red color of the solution,  $\text{KMnO}_4$  or  $\text{K}_2\text{Cr}_2\text{O}_7$  is suspected, reduction may be readily effected by acidifying with HCl, adding alcohol, and boiling. For most purposes, it will only be necessary to consider the presence of a large excess of  $\text{HNO}_3$  or *aqua regia*, because of their extensive use as solvents.

An excess of  $\text{HNO}_3$  is removed by evaporating the solution to about 1 cc., adding 3 cc. of concentrated HCl, and evaporating nearly to dryness. It can then be taken up with the aid of HCl and hot water.

An excess of *aqua regia* is disposed of by boiling the solution down to a small bulk, adding concentrated HCl and again evaporating to 1 cc.; it is then diluted with water and a few drops of HCl.

$\text{H}_2\text{S}$  as a Precipitating Agent. In precipitating the second group sulphides with  $\text{H}_2\text{S}$ , it is exceedingly important that the solution have a certain approximately definite acidity. If too great a concentration of acid is present, complete precipitation will be impossible, owing to the appreciable solubility of some of the sulphides in moderately strong HCl (notably those of Pb, Cd,

and Sn). On the other hand, if the acid concentration is too small, certain metals of the third group will also precipitate, ~~Zn~~, Zn, Ni, and Co.

By experiment it has been found that a concentration of 2.5 cc. of HCl (sp. gr. 1.2) in a volume of 100 cc. affords a satisfactory acidity for the separation of the second and third groups by H<sub>2</sub>S.

II

### Precipitation with H<sub>2</sub>S

The filtrate (1) from Group I. is made *slightly* alkaline with NH<sub>4</sub>OH and then *just* acid with dilute HCl (2); 2.5 cc. of concentrated HCl are then added, the solution is heated nearly to boiling and is treated with a rapid stream of H<sub>2</sub>S for a few minutes. Without filtering (3), add enough cold water to make the total volume 100 cc., cool to room temperature, and pass in H<sub>2</sub>S again until precipitation is complete. Filter, dilute the filtrate with  $\frac{1}{2}$  its volume of water, and treat again with H<sub>2</sub>S; now filter off any precipitate formed (4). The final filtrate should not give a precipitate when treated with H<sub>2</sub>S. The beaker containing the filtrate should be labeled Groups III.-V., *at once* placed on a wire gauze, and boiled until all the H<sub>2</sub>S is expelled (5).

The precipitate may consist of HgS, PbS, Bi<sub>2</sub>S<sub>3</sub>, CuS, CdS, As<sub>2</sub>S<sub>3</sub>, Sb<sub>2</sub>S<sub>3</sub>, SnS and S; it should be washed with water containing H<sub>2</sub>S and about 5 per cent. NH<sub>4</sub>NO<sub>3</sub> (6) until the washings are only faintly acid. Reject the washings.

### NOTES

1. A preliminary test for the second group should first be made on a small portion of the filtrate, in order to determine whether or not Group II. is present. If present, the entire filtrate should be treated with H<sub>2</sub>S in accordance with directions; if absent, the introduction and removal of H<sub>2</sub>S will thus be avoided. In that case pass to Scheme III.

2. The solution must be thoroughly stirred with a glass rod during the addition of the ammonium hydroxide and acid, and the acidity or alkalinity of mixture determined by means of litmus paper and not by the quantity of the reagent added. No attention need be given to precipitates which form, because these are either finally dissolved or converted by H<sub>2</sub>S into sulphides. If a large excess of acid is known to be present, it should be removed by evaporation and the solution then brought to the proper condition of acidity as directed in the procedure above.

3. The solution is not diluted at once to 100 cc. because of the possible presence of arsenic, which comes down best in a hot strongly acid solution. It is a good plan to mark with a label the level at which the beaker will hold 100 cc.; the dilution can then be made without resorting to a measuring cylinder.

4. The color of the  $H_2S$  precipitate sometimes affords an indication of the metals present. If black, it may be due to Pb, Cu, Hg, or to all of them; if yellow, to Cd, Sn(-ic), or As; if orange, to Sb. A yellow precipitate which is insoluble in  $(NH_4)_2S_x$  cannot be anything other than Cd; on the other hand, if the yellow precipitate dissolves completely in  $(NH_4)_2S_x$ , it must be either the sulphide of As or Sn(-ic), or both.

5. As  $H_2S$  in solution readily oxidizes in contact with air to S and  $H_2SO_4$ , and as the latter will precipitate alkaline earths, the necessity for immediately expelling the  $H_2S$  is apparent.

Keeping a glass rod in the beaker during the boiling will facilitate the removal of  $H_2S$  by preventing dangerous bumping, with a consequent loss of liquid. The completeness of the expulsion of the  $H_2S$  may be determined by holding a piece of filter paper moistened with lead acetate in the escaping vapor.

6. The precipitate is washed with  $H_2S$  water to prevent the oxidation of the sulphides to sulphates, which, with the exception of  $PbSO_4$ , are all soluble in water.  $NH_4NO_3$  is added to prevent the precipitate from going into the colloidal state and then passing through the filter.

The separation of Group II. into two divisions is based on the difference of behavior of the sulphides towards  $(NH_4)_2S_x$ .

Division II. A (the copper group) includes those sulphides which are insoluble in  $(NH_4)_2S_x$ ; these are Hg, Pb, Bi, Cu, and Cd.

Division II. B (the tin group) includes those sulphides which are soluble in  $(NH_4)_2S_x$  with the formation of thio salts. The separation, however, is not sharp, which is due to the slight solubility of CuS in  $(NH_4)_2S_x$ . CuS is practically insoluble in  $Na_2S_x$ , but the latter quite appreciably dissolves HgS. For all practical purposes, the separation with  $(NH_4)_2S_x$  is sufficiently complete.

In the analysis of the  $H_2S$  precipitate it is sometimes just as well to assume the presence of both divisions and to treat the *well-washed* precipitate at once with  $(NH_4)_2S_x$ , as directed in paragraph 3. In most cases, however, it is preferable to make the following preliminary tests.

*Preliminary examination of the H<sub>2</sub>S precipitate to determine the presence of—*

(1) Division A (copper group). By means of a glass spatula, put a very small amount of the precipitate into a small evaporating dish; add about 15 drops of (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub> diluted with an equal quantity of water. Break up the precipitate with a glass rod, and warm gently with constant stirring for a minute (*do not boil*). If the precipitate completely dissolves, the Cu group is absent and the main precipitate is analyzed for the Sn group only (Scheme II. B). If a residue remains (1), the copper group is present.

(2) Division B (tin group). Twice pass about 10 drops of (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub>, diluted with an equal volume of water, through the precipitate, which has been *thoroughly* washed and from which most of the water has drained; catch the liquid which passes through in a test tube (2) and just acidify with dilute HCl. In another test tube, *just* acidify with dilute HCl an equal portion of (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub>, diluted as above, and compare the results. A colored precipitate in the first tube which is different from that of the second proves the presence of the Sn group (3). If the two tubes present the same appearance after acidification, the absence of the Sn group is proved.

### (3). Separation of the Divisions of Group II.

If both divisions are shown to be present by the above tests, the entire precipitate is treated in a small beaker (50 cc. capacity) (4) with 10 cc. of (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub> diluted with 5 cc. of water; the mixture is thoroughly stirred, warmed for several minutes, and filtered (5). The residue on the filter may consist of HgS, PbS, Bi<sub>2</sub>S<sub>3</sub>, CuS, CdS and S. The filtrate may contain the thio salts of As, Sb, and Sn. A warm mixture of 2 cc. of (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub> and an equal volume of water is poured on the residue (6), and the liquid which passes through is united with the filtrate containing the thio salts of Division B, which is then analyzed according to Scheme II. B. The residue is washed twice with hot water containing 5 per cent. NH<sub>4</sub>NO<sub>3</sub> and is then analyzed according to Scheme II. A. The washings are rejected.

## NOTES

1. A residue of S is not to be taken as indicating the presence of the Cu group.
2. If the precipitate has not been washed free of acid, the latter will decompose the  $(\text{NH}_4)_2\text{S}_x$ , with the separation of S. If considerable acid is present, all of the  $(\text{NH}_4)_2\text{S}_x$  will be decomposed, with the result that the liquid which drains through the filter will be colorless and will fail to react with HCl. To remedy this, add more  $(\text{NH}_4)_2\text{S}_x$ , preferably diluted with  $\text{NH}_4\text{OH}$ , until a colored filtrate is obtained.
3. Because of the slight solubility of  $\text{CuS}$  in  $(\text{NH}_4)_2\text{S}_x$ , a liver-colored precipitate is sometimes obtained in acidifying the  $(\text{NH}_4)_2\text{S}_x$  solution.
4. If the quantity of the precipitate is small, it may be treated on the filter with  $(\text{NH}_4)_2\text{S}_x$ , using small portions at a time and allowing each portion to drain through before adding a fresh portion; in this way a maximum of extraction with the minimum amount of solvent is secured. If water is used in transferring the precipitate to a beaker, it must be carefully poured off before adding the  $(\text{NH}_4)_2\text{S}_x$ .
5. If the precipitate shows a tendency to pass through the filter in the colloidal condition, add several grams of  $\text{NH}_4\text{NO}_3$ , warm, stir, and refilter.
6. This further treatment of the residue with dilute  $(\text{NH}_4)_2\text{S}_x$  is given to insure the complete extraction of the As, Sb, and Sn

## Outline of the Separation of the Metals of Group II. A

Of the sulphides of Group II. A, only  $\text{HgS}$  is insoluble in hot dilute  $\text{HNO}_3$ ; the addition of this reagent to the mixed sulphides will therefore result in the solution of all the sulphides as nitrates, with the exception of  $\text{HgS}$ , which will be left behind as an insoluble residue. If, now, to the filtrate containing the nitrates of Pb, Bi, Cu, and Cd we add  $\text{H}_2\text{SO}_4$ , we should expect the Pb to precipitate as  $\text{PbSO}_4$ ; for Pb is the only metal of this group whose sulphate is insoluble in water. It is, however, appreciably soluble in nitric acid, and as the filtrate contains an excess of this acid, its removal is necessary if complete precipitation of the Pb as sulphate is desired. This is accomplished by adding concentrated  $\text{H}_2\text{SO}_4$  and evaporating the solution until  $\text{SO}_3$  fumes appear; it is then diluted with water and the  $\text{PbSO}_4$  is filtered off. The filtrate will now contain Bi, Cu, and Cd as sulphates, and an excess of  $\text{H}_2\text{SO}_4$ . A glance at the reactions of the salts of these metals shows that  $\text{NH}_4\text{OH}$  precipitates all three of them, but that Bi is the only one whose

hydroxide is insoluble in excess. If, therefore, an excess of  $\text{NH}_4\text{OH}$  is added to the filtrate from the  $\text{PbSO}_4$ ,  $\text{Bi}(\text{OH})_3$  will be precipitated and may be separated from the remaining two metals by filtration. The ammoniacal filtrate will be colored blue if Cu is present. Cu and Cd may be separated by taking advantage of the difference of behavior of their double cyanides towards  $\text{H}_2\text{S}$ . The double cyanides are formed by adding KCN to the ammoniacal solution until the blue color is discharged; the passage of  $\text{H}_2\text{S}$  into this solution precipitates only the Cd as yellow sulphide.

### SCHEME II. A

The residue from the  $(\text{NH}_4)_2\text{S}_2$  treatment may consist of  $\text{HgS}$ ,  $\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{CuS}$ , and  $\text{CdS}$ . Wash the precipitate into a small beaker, pour off the water, add 15-30 cc. of dilute  $\text{HNO}_3$  and heat with constant stirring (1); boil for one and a half minutes, and filter.

<p>Residue may be <math>\text{HgS}</math> (black) or <math>2 \text{HgS} \cdot \text{Hg}(\text{NO}_3)_2</math> (white) + S (2). Wash with water. Transfer ppt. to a small evap. dish; add 4 cc. <i>aqua regia</i>, and boil till all but S dissolves. Boil a little longer to expel <math>\text{Cl}</math>, dilute with 1 cc. of water, and filter. To filtrate add a few drops of <math>\text{SnCl}_2</math>; a white ppt., turning gray to black, proves the presence of Hg.</p>	<p>Filtrate may contain <math>\text{Pb}(\text{NO}_3)_2</math>, <math>\text{Bi}(\text{NO}_3)_3</math>, <math>\text{Cu}(\text{NO}_3)_2</math>, <math>\text{Cd}(\text{NO}_3)_2</math> + excess of <math>\text{HNO}_3</math>. Transfer to an evap. dish, add 5 cc. of conc. <math>\text{H}_2\text{SO}_4</math>, and evaporate under a hood until <math>\text{SO}_3</math> fumes are given off (3); cool and <i>cautiously</i> pour the contents of dish into a beaker containing 25 cc. of water. Rinse what remains in the evap. dish with a little water into the same beaker; stir, allow to settle, and filter.</p>
<p>Residue is <math>\text{PbSO}_4</math> (4). Wash once with water, and treat the ppt. on the filter with 10 cc. of a boiling solution of <math>\text{NH}_4\text{C}_2\text{H}_8\text{O}_2</math>. Catch filtrate in a test tube, add 2 cc. acetic acid and 1 cc. <math>\text{K}_2\text{CrO}_4</math>. A yellow ppt. confirms the presence of Pb.</p>	<p>Filtrate contains <math>\text{Bi}_2(\text{SO}_4)_3</math>, <math>\text{CuSO}_4</math>, <math>\text{CdSO}_4</math> + excess of <math>\text{H}_2\text{SO}_4</math>. Add <math>\text{NH}_4\text{OH}</math> to alkaline reaction and then in slight excess. A deep blue coloration proves the presence of Cu (5). Allow any ppt. which forms at the same time to settle and filter.</p>
	<p>Residue is <math>\text{Bi}(\text{OH})_3</math> (6). Wash with water; dissolve ppt. on the filter with about 5 drops of conc. <math>\text{HCl}</math>, and catch drops in a clean beaker. Add 50 cc. of water, warm, and allow to stand for a few minutes; a white ppt. or cloudiness is <math>\text{BiOCl}</math> (7).</p>

## NOTES ON SCHEME II. A

1. Stirring while heating with dilute  $\text{HNO}_3$  is important because of the tendency of the S, which separates in a plastic condition, to inclose portions of the sulphides, with the result that the latter are protected from the solvent action of the acid.

2. Besides the substances mentioned, the residue may consist of a little  $\text{PbSO}_4$  resulting from the oxidation of  $\text{PbS}$  by the use of strong  $\text{HNO}_3$  or the long-continued action of the dilute acid. But, as  $\text{PbSO}_4$  is somewhat soluble in hot dilute  $\text{HNO}_3$ , enough Pb passes into solution for its detection in the next operation.

A black residue is not to be taken as proof of the presence of Hg; it may be sulphur mechanically inclosing small quantities of the black sulphides, as  $\text{PbS}$ ,  $\text{CuS}$ , and  $\text{Bi}_2\text{S}_3$ . Consequently the residue after the  $\text{HNO}_3$  treatment, whether it is black or white, must be tested for Hg.

3. The object of evaporating the solution until  $\text{SO}_3$  fumes result is to completely remove the  $\text{HNO}_3$ , which has a solvent action on the  $\text{PbSO}_4$ . As the boiling point of concentrated  $\text{HNO}_3$  is  $120^\circ \text{C}$ . and the fuming point of  $\text{H}_2\text{SO}_4$  is  $250^\circ \text{C}$ ., it is evident that all the  $\text{HNO}_3$  will have been removed when the solution is boiled until dense white fumes of  $\text{SO}_3$  are given off. The student should not look for  $\text{SO}_3$  fumes until the bulk of his solution has been reduced to about 3 cc. If he is unable to recognize these fumes with certainty, he should show his results to his instructor before proceeding with the next step. Unless this operation is properly conducted, it will not be possible to completely separate the Pb, with the result that the tests for Bi and Cd will be interfered with.

4.  $\text{PbSO}_4$  is a heavy white powder; a white coarsely crystalline precipitate (a basic sulphate of Bi) sometimes separates, hence the necessity of making a confirmatory test for Pb. Where the amount of  $\text{PbSO}_4$  is very small, it can be made distinctly visible by collecting it in the center by means of a rotary motion imparted to the beaker.

5. The deep blue solution produced by an excess of ammonium hydroxide is sufficiently sensitive for the detection of Cu. A much more delicate test consists in acidifying a portion of the solution with acetic acid and adding  $\text{K}_4\text{Fe}(\text{CN})_6$ ; a brown precipitate or coloration proves the presence of Cu.

6. The formation of a white precipitate at this point is not proof of the presence of Bi; for if all the Pb had not been removed in the previous operation it will precipitate here. A confirmatory test for Bi must therefore always be made.

7. It frequently happens that a precipitate or cloudiness is not obtained even when Bi is present. This is due to the presence of an excess of acid, which reverses the direction of the reaction:  $\text{BiCl}_3 + \text{H}_2\text{O} \rightleftharpoons \text{BiOCl} + 2 \text{HCl}$ . This may be remedied by adding  $\text{NH}_4\text{OH}$  drop by drop to neutralize the excess of acid, care being taken, however, to keep the solution acid.

Another confirmatory test for Bi consists in pouring on the thoroughly washed white precipitate of  $\text{Bi}(\text{OH})_3$  a solution of  $\text{Na}_2\text{SnO}_3$  (prepared by adding NaOH to 1 cc. of  $\text{SnCl}_4$  till the precipitate which first forms dissolves), when if Bi is present it will be blackened due to the precipitation of metallic Bi.

8. The presence of Hg or Pb in the solution to be tested for Cd will yield a black precipitate when  $\text{H}_2\text{S}$  is passed into the solution. A little Hg may find its way into the solution if the original  $\text{H}_2\text{S}$  precipitate had not been thoroughly washed free from HCl or chlorides; the latter, on boiling with  $\text{HNO}_3$ , will yield *aqua regia*, which dissolves some of the  $\text{HgS}$ . The presence of Pb is due to its incomplete removal in the previous operation. A black precipitate obtained with  $\text{H}_2\text{S}$ , in testing for Cd, may be examined for this metal by filtering the precipitate, thoroughly washing it with hot water, and finally treating it with hot sulphuric acid (1 pt. of conc. acid to 4 pts. of water) on the filter. The dilute  $\text{H}_2\text{SO}_4$  dissolves the  $\text{CdS}$  and leaves on the filter the  $\text{HgS}$  and  $\text{PbS}$ ; the latter may be entirely changed to  $\text{PbSO}_4$ . If the filtrate is now *largely diluted* with water and treated with  $\text{H}_2\text{S}$ , a yellow precipitate of  $\text{CdS}$  will be formed if Cd is present.

#### Outline of the Analysis of Group II. B (the Tin Group)

The insolubility of  $\text{As}_2\text{S}_3$  in hot concentrated HCl is made use of to separate it from the sulphides of Sb and Sn; the latter two dissolve in this acid, forming the corresponding chlorides with an evolution of  $\text{H}_2\text{S}$ . The residue, after filtration, is taken into solution with concentrated  $\text{HNO}_3$ ; and the presence of arsenic, now in the form of arsenic acid, is confirmed by its precipitation with  $\text{AgNO}_3$  in a neutral solution as  $\text{Ag}_3\text{AsO}_4$ . When the  $\text{As}_2\text{S}_3$  is removed by filtration, the filtrate will contain the Sb and Sn as chlorides and an excess of  $\text{H}_2\text{S}$ . As the tests for Sb and Sn can be made in the presence of each other, it is needless to effect their separation. The filtrate, after boiling to expel the  $\text{H}_2\text{S}$ , is divided into two portions.

An iron nail is placed in the first portion and the liquid warmed. The iron acts on the acid present, liberating hydrogen, which reduces  $\text{SnCl}_4$  to  $\text{SnCl}_2$  and at the same time precipitates the Sb in the metallic state. The filtered solution, containing  $\text{SnCl}_2$ , is then tested with  $\text{HgCl}_2$  solution.

The second portion is tested for Sb by the galvanic action of the electric couple (Pt and Zn), which causes the antimony to precipitate as a black deposit on the platinum.

## SCHEME II. (TIN GROUP)

The filtrate obtained after treating the  $H_2S$  precipitate with  $(NH_4)_2S_2$  will contain the thio salts of the metals of this group; viz.,  $(NH_4)_2AsS_4$ ,  $(NH_4)_2SbS_4$ ,  $(NH_4)_2SnS_4$  and excess  $(NH_4)_2S_2$ . Just acidify with dilute HCl (1) and filter; reject the filtrate.

The residue will consist of  $As_2S_5$ ,  $Sb_2S_5$ ,  $SnS_2$ , ( $CuS$ ?), and S.

Transfer the precipitate to a small beaker, add 10 cc. of concentrated HCl, and heat gently to boiling (2), with constant stirring, for about 5 minutes. Dilute with an equal volume of water and filter.

Residue is  $As_2S_5 + S$  (3). Wash with hot water until the washings after boiling to expel  $H_2S$  give only a faint reaction with  $AgNO_3$ . Reject washings. Transfer ppt. to an evap. dish (if water is used in transferring ppt., pour it off after ppt. settles). Add 3-5 cc. of conc.  $HNO_3$ , stir, and heat gently until no more brown fumes are given off, and until the excess  $HNO_3$  is expelled. Dilute with 3 cc. of water and filter through a small filter. Wash filter with 1 cc. of water, catching filtrate and washings in a test tube. Add 5 cc. of  $AgNO_3$  (4); filter if a precipitate forms. To the clear solution or filtrate add one drop of phenolphthalein and then render just alkaline with  $NH_4OH$ . Now add 5% acetic acid drop by drop with shaking until the resulting mixture is faintly acid. A chocolate-colored ppt. of  $Ag_3AsO_4$  confirms the presence of arsenic (5).

Filtrate may contain  $SbCl_4$ ,  $SnCl_4$  + excess HCl +  $H_2S$ . Boil until the  $H_2S$  is completely expelled (6). Divide the solution into 2 portions. In the 1st portion, test for Sn by warming with an iron nail for 3 minutes. Filter rapidly (7) into a test tube containing 2-3 drops of  $HgCl_2$ ; a white ppt., which may turn gray or black, proves the presence of Sn. In the 2nd portion, test for Sb. Pour it into a small evap. dish containing Pt foil in contact with a piece of Sn or Zn. A black stain on the Pt (8), which is insoluble in  $NaBrO$ , is Sb.

## NOTES TO SCHEME II. B

1. An excess of acid is to be avoided because of the solubility of  $SnS_2$  in even moderately dilute acid.
2. The mixture must not be boiled, else some  $As_2S_5$  is apt to go into solution.
3. The separation of As from Sb and Sn sulphides by the use of hot concentrated HCl is not always very sharp. With mixtures consisting of a small

amount of As and a relatively large quantity of Sb, the insoluble residue may contain enough  $Sb_2S_3$  to give it a red color; therefore a red residue must always be examined for As.

**4.** If all the HCl had not been removed by washing, the addition of  $AgNO_3$  will yield a white precipitate of  $AgCl$ ; if this precipitate is large in amount, more  $AgNO_3$  should be added before filtering to insure an excess of the latter in the filtrate.

**5.** The test for arsenic with  $AgNO_3$  depends upon the formation of  $Ag_3AsO_4$ , which only forms in a strictly neutral solution; if too much acetic acid is added, precipitation will fail, because of the ready solubility of  $Ag_3AsO_4$  in acids as well as in alkalies. To remedy this, carefully neutralize the excess of acid by the addition of dilute  $NH_4OH$ .

**6. Test escaping vapors with lead acetate paper.**

**7.** By this procedure the  $SnCl_4$  is reduced to  $SnCl_2$ ; as the latter rapidly oxidizes on exposure to air, particularly in a hot solution, the necessity of rapidly filtering into a test tube containing the reagent is apparent.

**8.** If much Cu and little or no Sb are present, a dark red stain, easily distinguished from a black stain, will be produced.

The cleaning of the Pt foil is easily accomplished by first washing it with water and then pouring on it concentrated  $HNO_3$ .

### Reactions of Metals of Group III

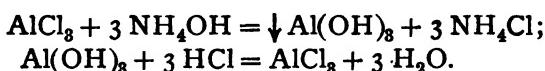
The metals of this group are distinguished from those of the first and second groups by the fact that they are not precipitated by  $H_2S$  from solutions containing 2.5 per cent. of hydrochloric acid, sp. gr. 1.2. They are associated together in one group because of their common property of being completely precipitated by  $(NH_4)_2S$  in solutions alkaline with ammonium hydroxide in the presence of  $NH_4Cl$  (distinction from Groups IV. and V.).

### ALUMINUM

The aluminum salts are nearly all colorless; the salts of the halogen acids, and the nitrate, sulphate, and acetate, are soluble in water.

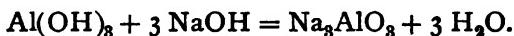
**1. Ammonium Hydroxide** throws down a white gelatinous precipitate of  $Al(OH)_3$ , slightly soluble in excess; on boiling, the dissolved hydroxide is reprecipitated. The presence of

$\text{NH}_4\text{Cl}$  diminishes the solvent action of ammonia on the hydroxide; hence, to completely precipitate aluminum by ammonia, the latter should be added only in slight excess and the mixture boiled until the liquid has but a faint odor of the reagent. When freshly precipitated,  $\text{Al}(\text{OH})_3$  is readily soluble in acids:—

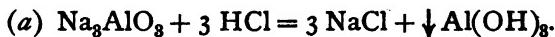


Aluminum hydroxide is also soluble in caustic alkalies (see 2).

2. Potassium or Sodium Hydroxide precipitates  $\text{Al}(\text{OH})_3$ , soluble in excess with the formation of alkali aluminate:—



On carefully neutralizing the alkaline solution of sodium aluminate with hydrochloric acid,  $\text{Al}(\text{OH})_3$  is reprecipitated:—



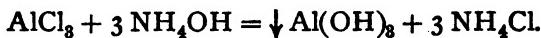
If an excess of acid is added, the precipitate which first forms is dissolved and we obtain:—



It is evident that if the original sodium aluminate solution is at once acidified with  $\text{HCl}$ , we shall get the net result of (a) and (b). Adding (a) and (b), and eliminating  $\text{Al}(\text{OH})_3$ , which appears on opposite sides, we get:—



If, now, we heat this solution to boiling and add ammonium hydroxide in faint excess, all the aluminum will be precipitated as the hydroxide:—

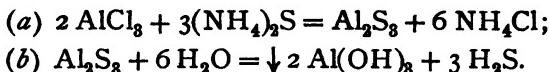


While the addition of a large excess of solid  $\text{NH}_4\text{Cl}$  will have the effect of precipitating  $\text{Al}(\text{OH})_3$  from the aluminate, the above process, viz., that of acidifying first with  $\text{HCl}$  and then rendering the resulting solution faintly alkaline with ammonium

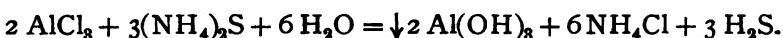
hydroxide, is the more common procedure and the one to be generally recommended.

It is important to remember that the direct addition of ammonium hydroxide to a sodium aluminate solution will not precipitate  $\text{Al}(\text{OH})_3$ .

~~3.~~ **Ammonium Sulphide** precipitates  $\text{Al}(\text{OH})_3$  and not the sulphide.  $\text{Al}_2\text{S}_3$  may be prepared in the dry way, but, on bringing it in contact with water, it at once hydrolyzes with the formation of the hydroxide and the evolution of  $\text{H}_2\text{S}$ . The action of  $(\text{NH}_4)_2\text{S}$  on solutions of aluminum salts may be represented as taking place in two steps:—



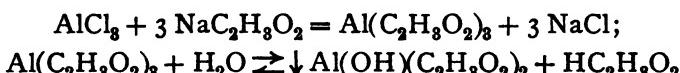
Adding (a) and (b), and eliminating  $\text{Al}_2\text{S}_3$ , we get as the equation for the final result:—



**4. Sodium Carbonate** also precipitates  $\text{Al}(\text{OH})_3$ .

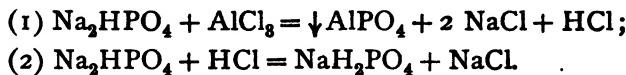
In the presence of non-volatile organic acids, as tartaric, citric, and malic acids, as well as certain organic matter containing ( $\text{OH}$ ) groups, as sugars and starch, ammonium hydroxide, sodium carbonate, and ammonium sulphide fail to precipitate aluminum salts.

**5. Alkali Acetate.** If an excess of alkali acetate is added to a slightly acid or neutral solution of an aluminum salt, and the mixture is largely diluted with water and boiled, a bulky precipitate of basic aluminum acetate will be thrown down:—

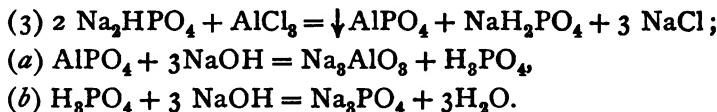


The reagent is, in fact, hot water, which hydrolyzes the weak salt  $\text{Al}(\text{C}_2\text{H}_5\text{O}_2)_3$ . Cooling the solution, or the presence of an excess of acetic acid, will have the effect of reversing the reaction, with the result that some of the precipitate will dissolve.

6. Disodium Phosphate yields with solutions of aluminum salts a gelatinous precipitate of  $\text{AlPO}_4$ , soluble in HCl and NaOH, but insoluble in acetic acid :—



Adding (1) and (2), and eliminating HCl, we get :—



Adding (a) and (b), and eliminating  $\text{H}_3\text{PO}_4$ , we get :—



7. Any aluminum compound, when strongly ignited in the air, is converted into  $\text{Al}_2\text{O}_3$ ; if this is moistened with a very dilute solution of  $\text{Co}(\text{NO}_3)_2$  and again strongly heated, a blue mass is obtained, due to the formation of cobalt aluminate. This reaction serves as an excellent confirmatory test for aluminum.

### CHROMIUM

The two principal oxides of chromium are  $\text{Cr}_2\text{O}_3$  and  $\text{CrO}_3$ . The former is basic and forms the various chromic \* salts by combining with acids, e.g.,  $\text{Cr}_2\text{O}_3 + 6 \text{HCl} = 2 \text{CrCl}_3 + 3 \text{H}_2\text{O}$ ; similarly by solution of  $\text{Cr}_2\text{O}_3$  in  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ ,  $\text{Cr}_2(\text{SO}_4)_3$  and  $\text{Cr}(\text{NO}_3)_3$  are respectively formed. In all these compounds chromium deports itself as a metal.  $\text{CrO}_3$ , on the other hand, is distinctly acid in character, being the anhydride of the hypothetical chromic acid,  $\text{H}_2\text{CrO}_4$ , the salts of which are known as chromates. The latter may be prepared by treating  $\text{CrO}_3$  with a base; thus, sodium chromate ( $\text{Na}_2\text{CrO}_4$ ) may be prepared by treating  $\text{CrO}_3$  with caustic soda:  $\text{CrO}_3 + 2 \text{NaOH} = \text{Na}_2\text{CrO}_4 + \text{H}_2\text{O}$ . In the chromates, chromium plays the

\* In this case the ending -ic refers to the element when acting as a base, i.e., its electro-positive properties dominate. This may perhaps best be shown by the valence as  $\text{Cr}^{III}$ , chromic, etc.

part of the *acid radical*  $\text{CrO}_4$ , the reactions of which are different from those given by Cr when a constituent of a chromic salt. An example will serve to illustrate this difference. Ammonium hydroxide, when added to a chromic salt, like  $\text{CrCl}_3$ , causes a precipitate of chromium hydroxide to form; when added, however, to a chromate, as  $\text{Na}_2\text{CrO}_4$ , no precipitate results. Further, if to chromic chloride we add a solution of barium chloride or lead acetate, no precipitate results; while if the same reagents are added to sodium chromate, yellow precipitates are formed, due to the formation of  $\text{BaCrO}_4$  and  $\text{PbCrO}_4$ , respectively.

The distinction is further noted when we compare the aqueous solutions of chromic salts and chromates; the former possess a green or violet color, while the latter are nearly always yellow.

Chromic salts ( $\text{Cr}^{\text{III}}$ ) are converted into chromates ( $\text{Cr}^{\text{VI}}$ ) by oxidation in an alkaline solution; conversely, chromates ( $\text{Cr}^{\text{VI}}$ ) are reduced to chromic salts ( $\text{Cr}^{\text{III}}$ ) by reduction in an acid medium.

The essential change may best be seen by considering only the oxides as taking part in the reactions; \* thus, the oxidation of a chromic salt to a chromate is given by the equation



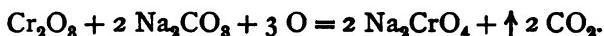
while the reduction of chromate to a chromic salt may be represented by



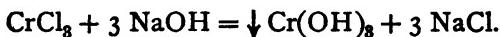
(a) **Oxidation of Chromic Salts to Chromates.** The oxidation is always carried out in an alkaline medium. In the dry way the oxidation may be accomplished by fusing a chromic compound with a mixture of  $\text{Na}_2\text{CO}_3$  (which supplies the alkali) and an oxidizing agent like  $\text{Na}_2\text{O}_2$ ,  $\text{KClO}_3$ , or  $\text{KNO}_3$  (which

\* As all chromic salts may be derived from  $\text{Cr}_2\text{O}_3$  by treatment of the latter with the appropriate acid, and as the valence of Cr is the same in this oxide and its salts we may conveniently represent all chromic salts in oxidation equations by  $\text{Cr}_2\text{O}_3$ . For a similar reason, all chromates may be represented in reduction reactions by  $\text{CrO}_3$ .

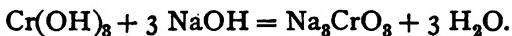
supplies the O). In its simplest form the equation for the oxidation is —



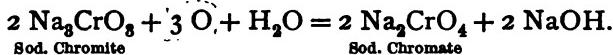
The oxidation may be carried out in an alkaline solution by using any one of the many oxidizing agents, such, for instance, as Br (or any halogen),  $\text{KMnO}_4$ , or  $\text{H}_2\text{O}_2$ . The alkali first precipitates chromic hydroxide :—



This then dissolves in excess, giving sodium *chromite* :—



The chromite is then oxidized by the oxidizing agent to chromate :—



When sodium dioxide ( $\text{Na}_2\text{O}_2$ ) is used, it is needless to first make the solution alkaline, because the sodium compound in contact with water is decomposed, yielding NaOH and O, according to the equation



An excess of  $\text{Na}_2\text{O}_2$  will therefore yield the excess of NaOH necessary to convert the chromic salt to sodium chromite, while the oxygen liberated at the same time will oxidize the chromite to chromate :—

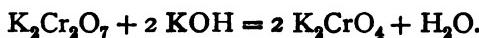


The oxidation by means of sodium dioxide is to be preferred to the other agents for the conversion of chromic compounds to chromate. In *every* case the oxidation is accompanied by a change in color from green to yellow.

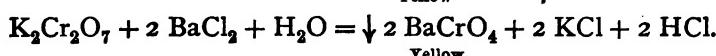
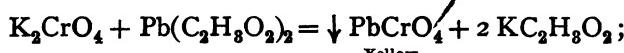
If a solution of a chromate is acidified, the color changes from a yellow to an orange-red, due to the formation of a dichromate :—



Conversely, if a base is added to a dichromate solution, the color changes from orange-red to yellow, due to the formation of a chromate :—



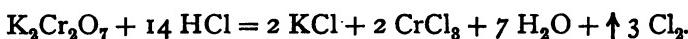
Both chromates and dichromates, when in solution, may be precipitated by solutions of Ba or Pb salts [distinction from chromic ( $\text{Cr}^{\text{III}}$ ) compounds] :—



Yellow

(b) Reduction of chromates to chromic compounds is effected in acid solutions by any one of the many reducing agents, e.g.,  $\text{H}_2\text{S}$ ,  $\text{HI}$ ,  $\text{SO}_2$ , concentrated  $\text{HCl}$ , and various organic substances, as alcohol and oxalic acid.

With concentrated  $\text{HCl}$  the reaction is —

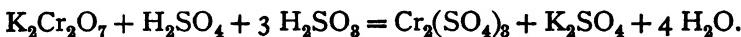


With  $\text{H}_2\text{S}$  the reduction takes place in accordance with the equation



In this case the green solution appears turbid from the separation of S.

With sulphurous acid the equation is —



In all the above cases the reduction is evidenced by a change in color from orange-red to green.

Other reaction for chromates will be given in Part II., dealing with the acids (see page 142).

### *The Chromic Salts*

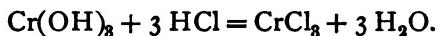
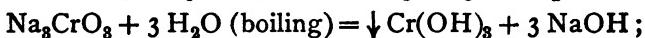
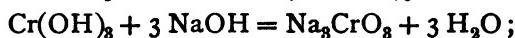
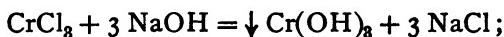
Of the common salts of chromium, the sulphate and the chloride exist in two forms: one is very readily soluble in water; while the other, which has been ignited, is neither soluble in

water nor acids. The nitrate exists in one form only and is easily soluble in water. All aqueous solutions of chromium salts have either a green or violet color, which varies with the concentration and other conditions. A solution containing as little as 1 part of chromium in 10,000 parts of water will have a distinct bluish green color.

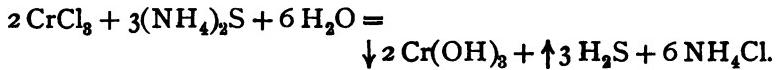
### *Reactions of the Chromic Salts*

1. **Ammonium Hydroxide** produces a greyish green or blue gelatinous precipitate of  $\text{Cr}(\text{OH})_3$ , soluble with difficulty in excess with the formation of a violet solution, from which, on boiling,  $\text{Cr}(\text{OH})_3$  is reprecipitated. The precipitate is easily soluble in acids and in sodium hydroxide (see 2).

2. **Sodium or Potassium Hydroxide** precipitates  $\text{Cr}(\text{OH})_3$ , soluble in excess in the cold to a green solution with the formation of sodium chromite; on boiling this solution,  $\text{Cr}(\text{OH})_3$  is reprecipitated (distinction from Al). The precipitate is easily soluble in acids.



3. **Ammonium Sulphide** precipitates  $\text{Cr}(\text{OH})_3$ , for  $\text{Cr}_2\text{S}_3$ , like  $\text{Al}_2\text{S}_3$ , is hydrolyzed by water with the formation of  $\text{Cr}(\text{OH})_3$  and the evolution of  $\text{H}_2\text{S}$ :—



4. **Sodium Carbonate** also precipitates the hydroxide. The presence of non-volatile organic acids, like tartaric and citric acids, as well as organic matter containing (OH) groups, as sugar and starch, interferes with reactions 1, 2, 3, 4, and 5.

5. **Disodium Phosphate** precipitates from solutions of chromic chloride green  $\text{CrPO}_4$ :—



The precipitate is easily soluble in inorganic acids, but is practically insoluble in cold dilute acetic acid, although it is soluble in a large excess of 50 per cent. acetic acid.

**6. Sodium Dioxide.** If a solution of a chromic salt is treated with a sufficient amount of sodium dioxide and boiled, all of the chromium will be converted into sodium chromate. The reaction may be represented by the following equations : —

- (1)  $3 \text{Na}_2\text{O}_2 + 3 \text{H}_2\text{O} = 6 \text{NaOH} + 3 \text{O}$  ;
- (2)  $\text{CrCl}_3 + 6 \text{NaOH} = \text{Na}_2\text{CrO}_8 + 3 \text{NaCl} + 3 \text{H}_2\text{O}$  ;
- (3)  $2 \text{Na}_2\text{CrO}_8 + 3 \text{O} + \text{H}_2\text{O} = 2 \text{Na}_2\text{CrO}_4 + 2 \text{NaOH}$ .

**7. If Sodium Acetate is added to a solution of a chromium salt,** no precipitate is produced even on boiling. If, however, the solution contains relatively large amounts of iron (ferric) and aluminum, the chromium will be almost completely precipitated as a basic acetate on boiling (compare the corresponding reaction for aluminum). Should the iron and aluminum be present in small and the chromium in relatively large amounts, the precipitation will be incomplete and in the filtrate will be found some of the Al, Cr, and Fe.

The *important deduction* from these facts is, that in the presence of a large amount of chromium it is necessary, in order to completely precipitate aluminum and iron as basic acetates, that one of the latter metals be present in large excess.

### IRON

Iron, as an electro-positive element, forms two distinct classes of salts ; viz., the ferrous compounds, in which iron is divalent, and the ferric salts, in which iron is trivalent. As the two classes exhibit a difference in behavior when treated with the same reagents, we shall consider them separately.

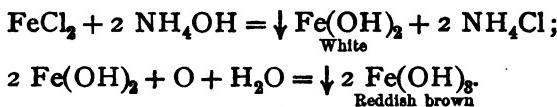
#### *The Ferrous Compounds*

When they contain "water of crystallization" the ferrous salts are green, and when anhydrous, they are white. The aqueous solutions, except when concentrated, are almost color-

less. Ferrous salts in solution are very unstable, for they rapidly absorb oxygen from the air and are converted into basic ferric salts, difficultly soluble in water. Oxidizing agents readily change ferrous salts to ferric compounds.

### *Reactions*

1. **Ammonium, Sodium, or Potassium Hydroxide** precipitates at first white gelatinous  $\text{Fe}(\text{OH})_2$ , which, on exposure to the air, is rapidly oxidized, becoming first dirty green, then black, and finally a reddish brown; the last is ferric hydroxide, and the other colors are doubtless due to varying mixtures of ferrous and ferric hydroxides.



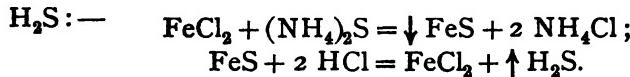
In the presence of much ammonium chloride, ammonium hydroxide fails to yield an immediate precipitate; but on exposure of the ammoniacal solution to the air, ferric hydroxide is finally thrown down. If the air is excluded, ammonium hydroxide does not precipitate ferrous salts in the presence of a sufficient quantity of ammonium salts (distinction from ferric salts).

The property of not being precipitated by ammonium hydroxide in the presence of a sufficient amount of ammonium salts is not peculiar to ferrous salts alone, but is shared alike by the salts of nickel, cobalt, manganese, zinc, and magnesium.\*

2. **Hydrogen Sulphide**, in acid solution, gives no precipitate. From neutral solutions a slight precipitate of  $\text{FeS}$  results; if, however, considerable sodium acetate is present, a larger, though still incomplete, precipitation is obtained. From alkaline solutions,  $\text{H}_2\text{S}$  completely precipitates the iron as black ferrous sulphide.

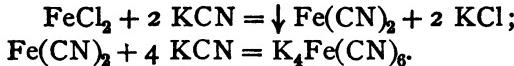
\* An explanation of this fact may be found in the *Theory of Electrolytic Dissociation* and the *Law of Mass Action*. The presence of  $\text{NH}_4\text{Cl}$  diminishes the concentration of the  $(\text{OH})$  ions derived from the ammonium hydroxide to such an extent as to yield with the ferrous iron present an amount of  $\text{Fe}(\text{OH})_2$  less than the solubility product of the latter.

3. **Ammonium Sulphide** precipitates black FeS, easily soluble in acids with the formation of a ferrous salt and evolution of



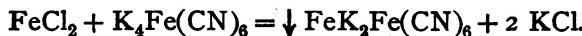
When moist, it readily oxidizes in the air, becoming first ferrous sulphate and finally brown basic ferric sulphate. To prevent this oxidation, the precipitate should be washed with water containing ammonium sulphide. The presence of ammonium chloride assists the precipitation.

4. **Potassium Cyanide** precipitates brown ferrous cyanide, soluble in excess with the formation of potassium ferrocyanide :—

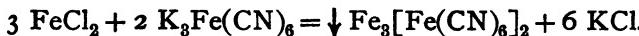


The solution of potassium ferrocyanide does not give any of the reactions of ferrous salts ; it is therefore not a ferrous salt, but the potassium salt of ferrocyanic acid,  $\text{H}_4\text{Fe}(\text{CN})_6$ . The group  $\text{Fe}(\text{CN})_6$  is an acid radical like  $\text{CrO}_4$  in chromates and differs distinctly in its behavior from iron, existing as the simple metallic component of salts.

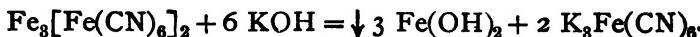
5. **Potassium Ferrocyanide** precipitates, in the complete absence of air, white  $\text{K}_2\text{Fe}^{\text{II}}\text{Fe}(\text{CN})_6$ ; under ordinary atmospheric conditions, however, a light blue precipitate is obtained, due to partial oxidation ; on prolonged exposure, it is completely converted into a dark blue precipitate of prussian blue :—



6. **Potassium Ferricyanide** produces even in very dilute solutions of ferrous salts a dark blue precipitate, known as Turnbull's blue, which is indistinguishable in color from prussian blue :—



The precipitate is insoluble in HCl, but is decomposed by caustic alkalies with the formation of ferrous hydroxide and alkali ferricyanide :—

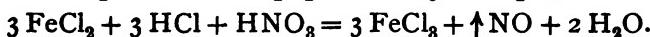


The ferricyanide at once oxidizes the ferrous hydroxide, so that the final products are  $\text{Fe(OH)}_3$  and  $\text{K}_4\text{Fe}(\text{CN})_6$ .

**7. Potassium thiocyanate** gives no reaction with ferrous salts (distinction from ferric salts).

**Oxidation of Ferrous to Ferric Salts.** It has been already stated that solutions of ferrous salts are very unstable, oxidizing gradually on exposure to air to ferric compounds. The oxidation can be more rapidly accomplished by the use of oxidizing agents in acid solution, as the halogens, *aqua regia*, a mixture of HCl and  $\text{KClO}_3$ , nitric acid, potassium permanganate, potassium dichromate, and hydrogen dioxide. The equations for the oxidation of ferrous salts by nearly all of these oxidizing agents have been given under *Oxidation and Reduction* (see page 25).

In oxidizing with nitric acid, the strong acid should be added drop by drop to the boiling acid solution of ferrous salt until no further darkening of the solution is evident. The oxidizing action of hydrogen dioxide and *aqua regia*, respectively, may be represented by the following equations :—



### Ferric Salts

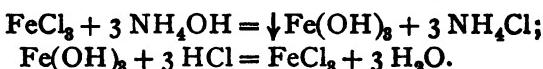
Most of the ferric salts, as the chloride, nitrate, and sulphate, yield solutions with a yellowish brown color, which varies in intensity with the concentration and temperature of the solution, as well as with the quantity of free acid present. The ferric ammonium alum,  $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24 \text{H}_2\text{O}$ , is violet. Ferric salts in dilute aqueous solutions are readily hydrolyzed, particularly on heating, with the formation of an insoluble basic ferric salt which dissolves on the addition of an acid :—



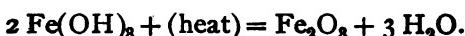
### Reactions

**1. Ammonium, Sodium, or Potassium Hydroxide** precipitates a reddish brown gelatinous precipitate of  $\text{Fe(OH)}_3$ . The precipi-

tate is unaffected by the presence of ammonium salts [distinction from  $\text{Fe}(\text{OH})_2$ ], and is soluble in acids, but is insoluble in an excess of sodium hydroxide (distinction from Al and Cr); it is also insoluble in an excess of ammonium hydroxide :—

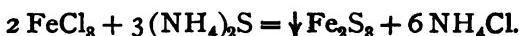


On ignition it yields  $\text{Fe}_2\text{O}_3$  :—



Ignited,  $\text{Fe}_2\text{O}_3$  is difficultly soluble in dilute acids, but dissolves on prolonged treatment with hot concentrated hydrochloric acid.

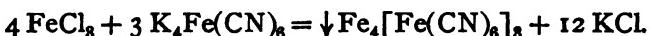
**2. Ammonium Sulphide** gives with acid solutions a precipitate consisting of  $\text{FeS} + \text{S}$ . From ammoniacal solutions, black ferric sulphide,  $\text{Fe}_2\text{S}_3$ , is precipitated :—



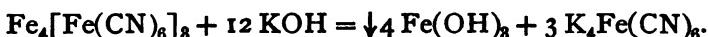
The precipitate is readily soluble in hydrochloric acid with the formation of ferrous chloride and the separation of sulphur :—



**3. Potassium Ferrocyanide** produces with ferric salts a blue precipitate known as prussian blue :—



The precipitate is insoluble in dilute HCl, but dissolves in oxalic acid, as well as in a great excess of the precipitant, with the formation of a blue solution. Prussian blue is decomposed by caustic potash, the products being ferric hydroxide and potassium ferrocyanide :—

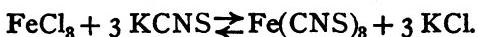


In making this test for iron, it is important that the solutions contain only a small amount of strong acid, as the latter would partially decompose the reagent with the formation of a small quantity of iron salt, which, reacting with the unchanged portion

of the reagent, would yield a blue coloration. Neutral solutions containing 1 part of iron in 500,000 parts of water will give this reaction. When only small amounts of iron are present, a blue or green coloration, instead of a blue precipitate, is obtained.

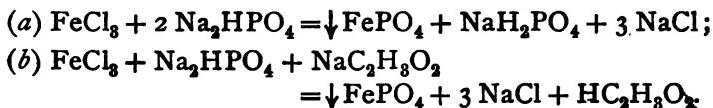
4. **Potassium Ferricyanide** does not precipitate ferric salts, but produces a brown coloration (distinction from ferrous salts).

5. **Potassium Thiocyanate** gives with solutions of ferric salts a deep red coloration, due to the formation of ferric thiocyanate, which is soluble in water :—



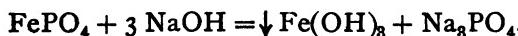
The reaction being reversible, its sensitiveness is increased by adding an excess of the reagent. As little as 1 part of iron in 1,600,000 parts of water can be detected by this reagent. The delicacy of the test may be further increased by adding a little pure ether and shaking; the ether extracts, and thus concentrates, the colored body. Nitric and chloric acids also give with the reagent a red coloration, but the latter, when due to these substances, is destroyed by adding alcohol and heating. Relatively large amounts of alkali acetate, organic acids, like tartaric, acetic, and oxalic, as well as phosphoric, arsenic, and boric acids, interfere with the reaction in neutral, though not in strongly acid, solutions. The addition of acid in making the test is therefore advisable. Mercuric chloride bleaches the red coloration.

6. **Disodium Hydrogen Phosphate** in neutral or slightly acid solutions of ferric salts containing a relatively large amount of sodium acetate, produces a buff-colored precipitate of ferric phosphate :—



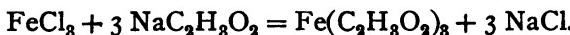
In (a) all the iron is precipitated but not all the phosphoric acid; in (b) both the iron and phosphoric acid are precipitated.

$\text{FePO}_4$  is insoluble in acetic acid, but readily dissolves in HCl. Caustic alkalies decompose it into  $\text{Fe(OH)}_3$  and  $\text{Na}_3\text{PO}_4$  :—

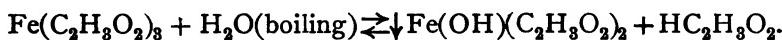


Treatment with ammonium hydroxide or hot water effects a partial hydrolysis into the hydroxide.

7. Sodium or Ammonium Acetate, when added in excess to a slightly acid solution of a ferric salt, causes the solution to take on a reddish brown color, due to the formation of ferric acetate :—

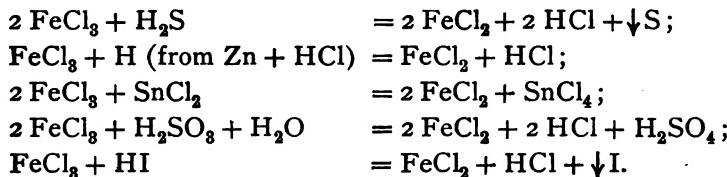


If this solution is largely diluted and boiled, all the iron will be precipitated as a basic acetate :—



The presence of non-volatile organic acids or sugar interferes with the precipitation of Fe in reactions 1, 6, 7.

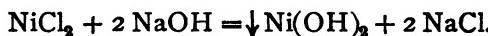
8. Reduction of ferric salts to ferrous may be readily effected in acid solution by reducing agents, as  $\text{H}_2\text{S}$ , nascent H,  $\text{SnCl}_2$ ,  $\text{H}_2\text{SO}_3$ , HI, and others. The following equations illustrate this :—



### NICKEL

When in the crystalline condition or in aqueous solutions, the nickel salts are green; when anhydrous, they are yellow. The green solutions can be rendered colorless by admixture with cobalt compounds in the proportion of 3 of nickel to 1 of cobalt.

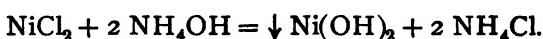
1. Potassium or Sodium Hydroxide precipitates green gelatinous  $\text{Ni(OH)}_2$ , insoluble in excess and not oxidized on exposure to air :—



The precipitate is readily soluble in acids ; also in ammonium hydroxide and ammonium salts. If the alkaline solution containing  $\text{Ni(OH)}_2$  in suspension is treated with bromine or chlorine and the mixture boiled, black nickel (-ic) hydroxide is formed :—



**2. Ammonium Hydroxide**, when considerably diluted and added in small quantity, causes a green turbidity, due to the formation either of a basic salt or the hydroxide :—

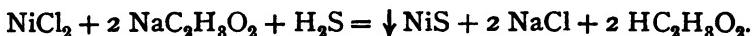


The precipitate is readily soluble in excess or in the presence of ammonium salts, with the formation of a blue solution containing a nickel ammonia salt :—

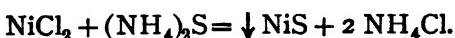


Therefore, in the presence of sufficient ammonium salts, Ni is not precipitated by ammonium hydroxide.

**3. Hydrogen Sulphide** yields no precipitate in solutions of nickel containing mineral acids or much acetic acid. If, however, the acetic acid solution contains a relatively large amount of sodium acetate, or if the solutions are rendered ammoniacal, hydrogen sulphide will completely precipitate the nickel as black nickel sulphide :—



**4. Ammonium Sulphide** gives with neutral or alkaline solutions of nickel salts a black precipitate of  $\text{NiS}$ , somewhat soluble in excess, especially in the presence of free ammonia, with the formation of a dark brown solution (distinction from Co). If this brown solution is acidified with acetic acid and boiled,  $\text{NiS}$  is reprecipitated. The presence of large quantities of ammonium salts prevents the solution of  $\text{NiS}$  in  $(\text{NH}_4)_2\text{S}$  solution.

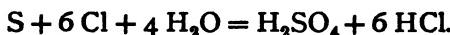


Nickel sulphide is practically insoluble in cold  $\text{HCl}$  (sp. gr. 1.02) (distinction from the sulphides of Mn, Zn, and Fe). It is also

insoluble in acetic acid, but is readily taken into solution on heating with *aqua regia* or concentrated nitric acid :—

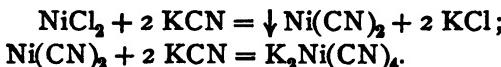


The sulphur, which separates in a plastic condition, often appears black because of the presence of some NiS inclosed in it. If the treatment with *aqua regia* is continued for some time, all the sulphide will be dissolved and the sulphur will be converted into sulphuric acid :—

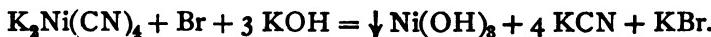


On exposure to air, moist nickel sulphide is oxidized to  $\text{NiSO}_4$ .

5. Potassium Cyanide gives a green precipitate of nickel cyanide, readily soluble in excess with the formation of a double cyanide :—

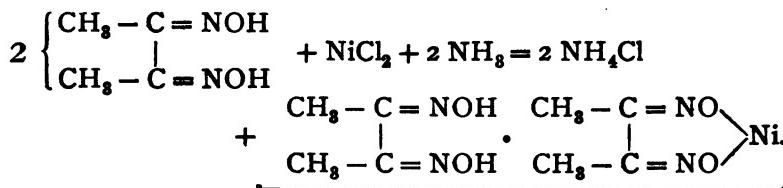


If the solution of the double cyanide is made strongly alkaline with  $\text{NaOH}$ , and then treated with bromine or chlorine and gently heated, decomposition of the double cyanide results with the precipitation of black nickel (-ic) hydroxide (distinction and method of separation from Co) :—



6. Potassium Nitrite, in dilute solutions of nickel salts acid with acetic acid, gives no precipitate (distinction and method of separation from Co).

7. Dimethylglyoxime. From solutions of nickel salts, alkaline with ammonia, an alcoholic solution of dimethylglyoxime will yield a voluminous red precipitate of the composition shown in the following equation :—



The presence of one part of nickel in 400,000 parts of water may be detected by this reagent. Cobalt salts do not give this reaction.

**8. Borax Bead Test.** A borax bead, when fused with a nickel compound in the oxidizing flame, is colored reddish brown, due to the formation of  $\text{Na}_2\text{Ni}(\text{BO}_2)_4$ . In the reducing flame, the nickel is reduced to the metallic state, imparting a gray color to the bead.

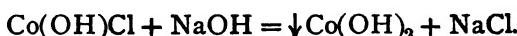
### COBALT

The cobalt salts, when in the crystallized condition or in aqueous solution, are reddish pink ; in the anhydrous form, they are usually blue. The concentrated aqueous solutions in the presence of HCl are also blue.

**1. Sodium Hydroxide** precipitates from cold solutions a blue basic salt :—



This is converted, on warming in contact with the alkali, to pink cobaltous hydroxide :—



The precipitate is insoluble in excess, but readily soluble in ammonium salts ; hence, the presence of ammonium salts in sufficient quantity interferes with the precipitation. On exposure to the air, the pink hydroxide oxidizes to black  $\text{Co(OH)}_3$  [resemblance to Fe(-ous) and Mn, and distinction from Ni] :—



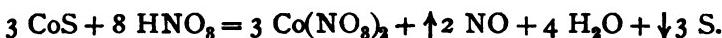
**2. Ammonium Hydroxide**, in the absence of ammonium salts, produces the same precipitate as in (1), but the latter readily dissolves in excess of the reagent to a brownish solution, which, on exposure to air or on boiling, changes to a red solution, due to the formation of a complex ammonia compound :—



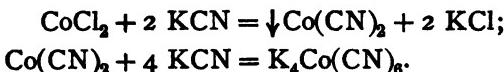
As in the case of Al, Cr, and Fe(-ous), the precipitation of Co as hydroxide is interfered with by the presence of non-volatile organic acids or sugar.

**3. Hydrogen Sulphide.** Same as with Ni.

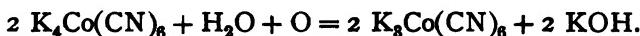
**4. Ammonium Sulphide** precipitates in neutral or alkaline solutions black CoS, insoluble in excess (distinction from Ni), insoluble in HCl (sp. gr. 1.02) and in acetic acid. It is soluble in *aqua regia* and concentrated nitric acid with the separation of sulphur :—



**5. Potassium Cyanide** gives in neutral solutions a light brown precipitate of cobaltous cyanide, easily soluble in excess to a brown solution with the formation of a double cyanide :—



The latter is similar to potassium ferrocyanide, hence it is called potassium cobaltocyanide. On warming the solution of the double cyanide for some time, it changes color to a bright yellow, due to oxidation to potassium cobalticyanide [similar to  $\text{K}_4\text{Fe}(\text{CN})_6$ ] :—



The reaction takes place more rapidly if sodium hydroxide and bromine or, what amounts to the same, NaBrO solution, is added to the solution of potassium cobaltocyanide. Nickel does not form the corresponding compound, but under these conditions it is converted into black insoluble  $\text{Ni}(\text{OH})_3$  (distinction and method of separation from Co).

**6. Potassium Nitrite** produces, when added in excess to a not too diluted solution of cobalt acidified with acetic acid, a yellow crystalline precipitate of potassium nitrocobaltate,  $\text{K}_8\text{Co}(\text{NO}_2)_6$ . With dilute solutions of cobalt, the mixture should be warmed and allowed to stand for at least twelve hours in order to get complete precipitation. The reaction may be represented as taking place in several stages :—

- $$(a) \text{CoCl}_2 + 2 \text{KNO}_3 = \text{Co}(\text{NO}_3)_2 + 2 \text{KCl};$$
- $$(b) 2 \text{KNO}_3 + 2 \text{HC}_2\text{H}_3\text{O}_2 = 2 \text{HNO}_3 + 2 \text{KC}_2\text{H}_3\text{O}_2;$$
- $$(c) 2 \text{HNO}_3 = \text{H}_2\text{O} + \text{NO} + \text{NO}_2;$$
- $$(d) \text{Co}(\text{NO}_3)_2 + \text{NO}_2 = \text{Co}(\text{NO}_3)_3;$$
- $$(e) \text{Co}(\text{NO}_3)_3 + 3 \text{KNO}_3 = \downarrow \text{K}_3\text{Co}(\text{NO}_3)_6.$$

The precipitate is somewhat soluble in water, but is practically insoluble in a solution saturated with a potassium salt. It is insoluble in alcohol and in an excess of  $\text{KNO}_3$  solution. Hence, for a rapid precipitation of cobalt as  $\text{K}_3\text{Co}(\text{NO}_3)_6$ , the solution of cobalt should be concentrated by evaporation, the mineral acid replaced by acetic, saturated with  $\text{KCl}$ , and then treated with an excess of  $\text{KNO}_3$  solution. If the mixture is now warmed and vigorously shaken, complete precipitation may be secured in a half hour.

7. **Nitroso- $\beta$ -naphthol**, dissolved in 50 per cent. acetic acid, yields with a hot solution of cobalt, preferably the chloride or sulphate acidified with hydrochloric acid, a voluminous red precipitate of cobalt-nitroso- $\beta$ -naphthol (distinction and method of separation from nickel, which, in  $\text{HCl}$  solution, does not give a precipitate).

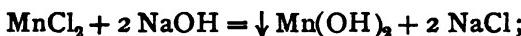
8. **A borax bead**, when fused with cobalt compounds either in the oxidizing or reducing flames, is colored blue. This test is not masked by the presence of moderate amounts of nickel.

### MANGANESE

The manganese salts, which may be formed by the solution of the oxide  $\text{MnO}$  in acids, are colored pink in the crystallized condition as well as in concentrated aqueous solutions. In the anhydrous state, with the exception of the sulphide, they are nearly all colorless.

#### *Reactions*

1. **Sodium or Potassium Hydroxide** produces with manganous salts a white precipitate of  $\text{Mn}(\text{OH})_2$ , which, on exposure to air, rapidly oxidizes, becoming brown :—



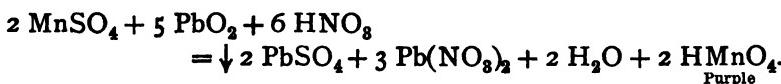
**2. Ammonium Hydroxide** yields with manganous solutions, in the absence of ammonium salts, a partial precipitation of white  $\text{Mn}(\text{OH})_2$ , oxidizing, as described in (1), to brown  $\text{Mn}_2\text{O}_3$ . In the presence of a sufficient amount of ammonium salts, no immediate precipitate forms; but, on exposure to air,  $\text{MnO}(\text{OH})_2$  is thrown down. The separation of manganese from any or all of the trivalent metals of this group by means of  $\text{NH}_4\text{Cl}$  and ammonium hydroxide is therefore incomplete. Non-volatile organic acids and sugar interfere with the precipitation of  $\text{Mn}(\text{OH})_2$ .

**3. Ammonium Sulphide** precipitates light pink hydrated manganous sulphide, which, on exposure to air, becomes dark brown, due to partial oxidation to  $\text{Mn}_2\text{O}_3$  :—



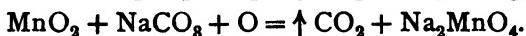
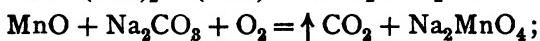
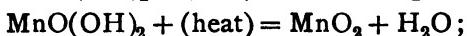
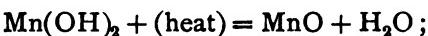
The precipitate is easily soluble in dilute acids (distinction from Ni and Co), even in acetic acid (distinction from Zn, as well as Ni and Co). The addition of ammonium chloride assists the precipitation, while the presence of oxalates and tartrates retards it. On boiling with a large excess of  $(\text{NH}_4)_2\text{S}$ ,  $\text{MnS} + \text{aq.}$  is changed to a less hydrated green sulphide of the formula  $3 \text{MnS} \cdot \text{H}_2\text{O}$ .

**4. Lead Dioxide and Nitric Acid.** If a very dilute solution of manganous salt, free from  $\text{HCl}$  or chlorides, is boiled with a gram of lead dioxide and a few cubic centimeters of concentrated nitric acid, and allowed to settle, the clear supernatant liquid will be colored purple, due to the formation of permanganic acid :—



This reaction is sufficiently delicate to detect a trace of manganese.

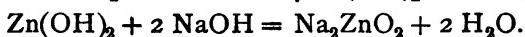
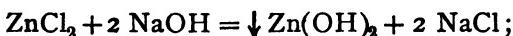
5. If a sodium carbonate bead is fused with a very small amount of a manganese compound in the oxidizing flame, or if the fused mass, while hot, is quickly dipped into a little powdered potassium chlorate, a bluish green or green mass will be formed, due to the formation of sodium manganate,  $\text{Na}_2\text{MnO}_4$  :—



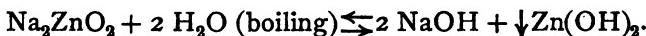
### ZINC

Most of the zinc salts are colorless; some are soluble in water, and the others are dissolved by acids.

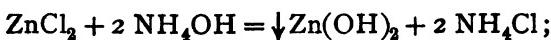
1. Sodium or Potassium Hydroxide precipitates white gelatinous zinc hydroxide, readily soluble in excess with the formation of sodium zincate [similar to Al, distinction from Fe(-ic) and Mn] :—



Unless the solution of the zincate contains a decided excess of NaOH, it will be decomposed on boiling with the reprecipitation of the hydroxide :—



2. Ammonium Hydroxide yields with solutions of zinc salts, in the absence of ammonium salts, a partial precipitation of zinc hydroxide, readily soluble in excess in the presence of ammonium salts with the formation of a complex ammonia salt :—



3. Hydrogen Sulphide, when passed into neutral solutions of zinc salts of inorganic acids, incompletely precipitates white zinc sulphide ( $\text{ZnS}$ ). A partial precipitation is also obtained

from solutions containing a small amount of free mineral acid. From solutions of zinc acetate, or from neutral solutions of salts of strong acids containing a moderate amount of sodium acetate,  $\text{H}_2\text{S}$  completely precipitates all the zinc as sulphide on boiling. Warming in the presence of alkali acetate promotes the precipitation :—

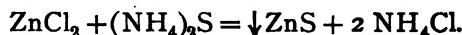


As  $\text{ZnS}$  is soluble in  $\text{HCl}$ , the precipitation in (a) is never complete. In equation (b),  $\text{NaC}_2\text{H}_3\text{O}_2$  has the effect of displacing the strong  $\text{HCl}$  by the weak acetic acid, in which  $\text{ZnS}$  is practically insoluble.\*

The tendency of  $\text{ZnS}$  to pass through the filter may be overcome by precipitating the sulphide in a nearly boiling solution of acetic acid containing a moderate excess of  $\text{NaC}_2\text{H}_3\text{O}_2$ , and filtering rapidly while hot. The precipitate may then be washed with hot water containing  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  or  $\text{NH}_4\text{NO}_3$  and  $\text{H}_2\text{S}$ . Zinc may also be precipitated by  $\text{H}_2\text{S}$  from sodium hydroxide solutions :—



**4. Ammonium Sulphide** yields in neutral and alkaline solutions a white precipitate of  $\text{ZnS}$  :—



$\text{ZnS}$  is readily soluble in dilute mineral acids, but is insoluble in acetic acid and in caustic alkalies.

**5. Any dried zinc compound, when moistened with dilute cobalt nitrate solution and ignited, will yield a green mass, due to the formation of a double oxide of Co and Zn (Thénard's green). This is an excellent confirmatory test for zinc and serves to distinguish zinc from aluminum.**

\* For an explanation of this fact according to the ionic theory and mass action law see page 15.

### Outline of the Method of Analysis for Group III

From an examination of the foregoing reactions, it becomes evident that if ammonia is added to a solution containing all the metals of this group, in the presence of a sufficient amount of ammonium chloride, all the trivalent metals (assuming the iron to be in the ferric state), viz., Fe, Al, and Cr, will be precipitated as hydroxides, while the remaining metals will be left in solution. This method would seem a desirable one for the separation of the third group into two divisions, and such a plan is, in fact, adopted by some chemists. We have not adopted this method for the reason that under the conditions given, manganese and zinc are not completely held in solution, and if present in small amounts may be wholly precipitated with the trivalent metals. However, the method gives fairly satisfactory results if the first precipitate of the hydroxides of Al, Cr, and Fe, containing some Mn and Zn, is dissolved and reprecipitated, and the second filtrate is united with the first.

Another reaction which may be utilized in separating the third group into two divisions is the basic acetate precipitation. This, it will be remembered, is based on the fact that in a nearly neutral solution containing a large excess of sodium acetate, a large amount of boiling water precipitates the basic acetates of ferric iron, aluminum, and chromium, while the remaining divalent metals are left in solution. This method of separation, one of the oldest in analytical chemistry, is exceedingly valuable in some cases, but it is not to be employed as a general method, because, as already pointed out (see under chromium, reaction 7), of its uncertainty in the presence of chromium.

The method adopted in this book consists in precipitating the entire group with  $(\text{NH}_4)_2\text{S}$  after rendering the solution alkaline with  $\text{NH}_4\text{OH}$ . Instead of  $(\text{NH}_4)_2\text{S}$ , the hot ammoniacal solution may be treated with a stream of  $\text{H}_2\text{S}$  until the precipitation is complete. In either case, the precipitate will consist of the hydroxides of aluminum and chromium, and the sulphides of iron, nickel, cobalt, manganese, and zinc. Since only the sulphides of Ni and Co are insoluble in HCl (1:9), it follows

that if the third group precipitate is treated with a sufficient amount of HCl (1 : 9) and filtered, there will remain on the filter the sulphides of Ni and Co, while in the filtrate will be found the chlorides of Al, Cr, Fe, Mn, and Zn. The residue, consisting of NiS and CoS, is next examined with a borax bead in the oxidizing flame, when, if not too great an amount of nickel is present, a blue bead will be obtained, indicating the presence of cobalt. To separate nickel and cobalt existing as sulphides, we must first get them into solution ; this is accomplished by heating with *aqua regia*, which converts the sulphides into soluble chlorides. From the solution of the chlorides, the cobalt may be separated from the nickel by precipitation with either potassium nitrite or nitroso- $\beta$ -naphthol. The nickel in the filtrate may be precipitated with NaOH and the resulting green hydroxide verified with a borax bead test. The main filtrate contains, besides the chlorides of Al, Cr, Fe, Mn, and Zn, an excess of HCl and H<sub>2</sub>S. The greater part of the HCl and all of the H<sub>2</sub>S are expelled by boiling down to a few cc. It will be recalled that in the cold, the hydroxides of Al, Cr, and Zn are soluble in excess of sodium hydroxide, forming, respectively, an aluminate, chromite, and zincate ; while the hydroxides of Fe (-ic) and Mn are insoluble. If an oxidizing agent like Br or H<sub>2</sub>O<sub>2</sub> is present, the chromite is converted into the yellow chromate, which is not precipitated on boiling. So that if a decided excess of NaOH and a little Na<sub>2</sub>O<sub>2</sub> are added to the main filtrate, which has been freed from H<sub>2</sub>S and the greater part of the HCl by evaporation to a few cc., and the mixture is boiled, diluted, and filtered, there will remain on the filter the hydroxides of Mn and Fe (-ic), while in the filtrate we should have sodium zincate, sodium aluminate, and sodium chromate ; the last will be evidenced by the yellow color which it imparts to the alkaline solution. In the residue the separation of Fe and Mn may be accomplished by dissolving the precipitate in HCl, nearly neutralizing the solution, and precipitating the Fe as basic acetate. From the filtrate, the Mn may be precipitated by adding Br and boiling, or by the addition of an excess of Na<sub>2</sub>O<sub>2</sub> or NaOH. When a rough estimation of the amount of Mn and Fe is not desired, separation is unneces-

sary, for we can readily identify each in the presence of the other. The presence of Mn may be determined by the characteristic green bead it gives when a little of the mixture is fused in a  $\text{Na}_2\text{CO}_3$  bead in the presence of an oxidizing agent; the iron may be detected by dissolving part of the precipitate in hot dilute HCl and adding a few drops of potassium ferrocyanide, when a blue precipitate of prussian blue will be obtained. The filtrate from the Mn and Fe precipitate will contain sodium chromate, sodium aluminate, and sodium zincate, as well as an excess of NaOH. If this solution is acidified with  $\text{HNO}_3$ , about three grams of  $\text{NH}_4\text{Cl}$  are added, and then it is rendered slightly alkaline with ammonium hydroxide, only the Al will be precipitated. The zinc does not precipitate because of the presence of  $\text{NH}_4\text{Cl}$ , while the chromium no longer acts as metal but as the acid radical ( $\text{CrO}_4$ ), and in consequence is not precipitated by ammonium hydroxide. The filtrate from the  $\text{Al}(\text{OH})_3$  will contain zinc, chromium, and a slight excess of ammonia. By rendering the solution acid with acetic acid and adding  $\text{BaCl}_2$ , all of the chromium will be precipitated as  $\text{BaCrO}_4$ . From the filtrate the Zn may be precipitated by  $\text{H}_2\text{S}$ .

#### Scheme of Analysis for Group III

This scheme is applicable only in the absence of non-volatile organic matter and interfering acids such as phosphoric acid.

The filtrate from Group II., having been boiled to remove the  $\text{H}_2\text{S}$ , contains, besides the metals of the succeeding group, an excess of HCl.

**Preliminary Test.** To a small portion of the filtrate from Group II. which has been freed from  $\text{H}_2\text{S}$ , add 2-3 drops of concentrated  $\text{HNO}_3$  and boil. Add about 0.5 g. of  $\text{NH}_4\text{Cl}$  and then ammonium hydroxide to alkaline reaction. A precipitate may be  $\text{Fe}(\text{OH})_3$  (red),  $\text{Al}(\text{OH})_3$  (white), or  $\text{Cr}(\text{OH})_3$  (greenish blue). If the amount of Mn in the solution is large, a small precipitate of  $\text{MnO}(\text{OH})_2$  (brown) may also be obtained. If no precipitate forms, the absence of Al, Cr, and Fe is proved. If a precipitate is obtained, it is rapidly filtered and to this filtrate,

or to the filtrate from Group II., in which ammonium hydroxide produces no precipitate,  $(\text{NH}_4)_2\text{S}$  is added; a precipitate proves the presence of one or more of the remaining members of Group III., viz., Ni, Co, Mn, and ~~Zn~~. The color of this precipitate sometimes affords an indication of the metals present. If it is black, Ni or Co, or both, are present; if white, Zn is present, and Ni and Co are absent. If pink, becoming brown on exposure, Mn is present; the latter may at once be verified by the  $\text{Na}_2\text{CO}_3$  bead +  $\text{KClO}_3$ . Failure to precipitate with  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{S}$  in the presence of a sufficient amount of  $\text{NH}_4\text{Cl}$  proves the absence of Group III. In that case pass to Scheme IV.

#### NOTES

1. As a solution containing 1 part of Cr in 10,000 parts of water shows a distinct bluish green coloration, a colorless solution need not be tested for Cr.

2. The  $(\text{NH}_4)_2\text{S}$  used in the preliminary testing for Group III., as well as that needed later in the preparation of the wash water for the Group III. ppt., should be made as needed by treating a little dil.  $\text{NH}_4\text{OH}$  with a stream of  $\text{H}_2\text{S}$  for several minutes.

3. Solutions of Ni and Co may be mixed in such proportions as to yield an almost colorless solution; an almost colorless filtrate from the ammonium hydroxide precipitate does not, therefore, prove the absence of Ni or Co.

#### SCHEME III

If the preliminary tests have shown the presence of Group III., the entire filtrate from Group II. is treated with 2 grams of  $\text{NH}_4\text{Cl}$  (1) rendered alkaline with  $\text{NH}_4\text{OH}$  and then 2 cc. of strong  $\text{NH}_4\text{OH}$  in excess are added (2). The mixture is heated and treated with a stream of  $\text{H}_2\text{S}$  until precipitation is complete. Stir vigorously with gentle heating for a minute (3) and filter on a fluted filter. [The filtrate (4) is at once made acid with acetic acid (5), boiled until all the  $\text{H}_2\text{S}$  is expelled (6), and filtered (7). The clear filtrate is received in a beaker, labelled "Groups IV. and V.", covered and reserved.] The main ppt. may consist of  $\text{Al}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$ ,  $\text{FeS}$ ,  $\text{NiS}$ ,  $\text{CoS}$ ,  $\text{MnS}$ , and  $\text{ZnS}$ . Wash once with hot water containing  $\text{NH}_4\text{Cl}$  and a little  $(\text{NH}_4)_2\text{S}$  (8), and discard washings. With the aid of a spatula, transfer ppt. to a beaker. Carry to a hood and add 60-80 cc. of HCl (sp. gr. 1.02), prepared by mixing 1 part of conc. HCl with 9 parts of water, stir thoroughly (without heating) for about a minute; allow to settle (9), and filter.

Residue is NiS + CoS + S (10). Wash on filter once with HCl (1 : 9) and reject washings. Test ppt. with borax bead in the O. F. A blue bead proves the presence of Co. Nickel may, however, be also present (11). A reddish brown bead proves the presence of Ni and the absence of a relatively large amount of cobalt. In either case, transfer ppt. to a small evaporating dish, carry to a hood, add 5-10 cc. of dil. *aqua regia*, and boil till all but a small amount of black S dissolves; evaporate *just* to dryness (12). Take up with 2 cc. of dil. HCl and an equal vol. of hot water; heat if necessary to effect solution. Filter through a very small filter into a test tube. Add NaOH drop by drop to the filtrate till a slight but permanent ppt. forms. Dissolve the ppt. in acetic acid and add about 3 cc. in excess (13).\* Saturate the solution with KCl (14) by adding the salt in small amounts and shaking after each addition until no more dissolves. Decant the clear solution into another test tube and to the latter add an equal vol. of KNO<sub>2</sub>. Allow the ppt. to stand with frequent shaking for about  $\frac{1}{2}$  hour and filter. Residue is K<sub>2</sub>Co(NO<sub>2</sub>)<sub>6</sub> (yellow). To filtrate add NaOH to alkaline reaction; a green ppt. (15) which yields a brown borax bead in the O. F. proves the presence of Ni.

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Filtrate contains AlCl<sub>3</sub>, CrCl<sub>3</sub>, FeCl<sub>3</sub>, MnCl<sub>2</sub>, ZnCl<sub>2</sub> + H<sub>2</sub>S + excess HCl. Boil down in a large evap. dish under hood to about 1 cc. (16); dilute with 10 cc. of water, render strongly alkaline with *clear* NaOH solution, and add (under hood and with caution) 2 g. of Na<sub>2</sub>O<sub>2</sub> (17). Dip finger into solution, rub on thumb; a greasy feel indicates solution is sufficiently alkaline; if not, add more Na<sub>2</sub>O<sub>2</sub>. Boil with constant stirring for about 1 minute, add 10 cc. of water, and filter.

\* If a solution of dimethylglyoxime is available, proceed from this point as follows: Divide the solution into two equal portions. First portion test for cobalt by adding an equal volume of KNO<sub>2</sub> solution and warming. A yellow precipitate is K<sub>2</sub>Co(NO<sub>2</sub>)<sub>6</sub>. Confirm with borax bead. Second portion test for nickel by rendering the solution alkaline with NH<sub>4</sub>OH and adding 1 cc. of dimethylglyoxime. A red precipitate proves the presence of nickel.

**Residue is**  $\text{Fe(OH)}_3$  +  $\text{MnO}_2 \cdot x\text{H}_2\text{O}$  (18). Wash with hot water.  
**Test for Mn.** On a  $\text{Na}_2\text{CO}_3$  bead take up a very small amount of the ppt. and heat; while hot dip into a little powdered  $\text{KClO}_3$  contained in a small watch glass. A green or bluish green mass of  $\text{Na}_2\text{MnO}_4$  proves the presence of Mn.

**Test for Fe.**

Transfer part or all of the ppt. to a test tube, add dil. HCl and heat till solution takes place. If Mn has been shown to be present, boil until all the chlorine is expelled. Cool and add a few drops (19) of  $\text{K}_4\text{Fe}(\text{CN})_6$ ; a blue ppt. proves the presence of Fe.

**Filtrate (20)** may contain  $\text{Na}_3\text{AlO}_2$ ,  $\text{Na}_2\text{CrO}_4$ ,  $\text{Na}_2\text{ZnO}_2$  + excess NaOH. Render slightly acid with *cautious* addition of conc.  $\text{HNO}_3$ ; add 3 grams of  $\text{NH}_4\text{Cl}$  (21), heat to boiling, and then add  $\text{NH}_4\text{OH}$  drop by drop with constant stirring until the resulting alkaline solution has only a faint odor of ammonia (22). (If too much  $\text{NH}_4\text{OH}$  is added, boil off the excess and filter.)

**Residue is**  $\text{Al}(\text{OH})_3$  (27). Wash with hot water several times and confirm by winding Pt wire around a portion of the paper and ppt., moistening with several drops of  $\text{Co}(\text{NO}_3)_2$  (23) and igniting strongly. A blue mass is cobalt aluminate,  $y\text{Al}_2\text{O}_3 \cdot x\text{CoO}$ .

**Filtrate** may contain  $(\text{NH}_4)_2\text{CrO}_4$ ,  $\text{Zn}(\text{NH}_3)_4\text{Cl}_2$  + excess  $\text{NH}_4\text{OH}$ . Acidify with acetic acid, add a gram of  $\text{NaC}_2\text{H}_8\text{O}_2$  (25), and heat to boiling. To the hot solution add  $\text{BaCl}_2$ , drop by drop, till precipitation is complete; allow to settle and filter through a double filter.

**Residue** is yellow  $\text{BaCrO}_4$  (24). Confirm by treating ppt. on filter with hot dil.  $\text{HNO}_3$ . Catch filtrate in a test tube. Cool thoroughly. Add 1 cc. of ether and 1 cc. 3%  $\text{H}_2\text{O}_2$  and shake. A blue color in the ether layer proves the presence of Cr.

**Filtrate**, which should be perfectly clear (26), is treated with  $\text{H}_2\text{S}$ . A white ppt. is  $\text{ZnS}$  (27). To confirm the presence of Zn, filter, wash with hot water, and then moisten with 2 drops of  $\text{Co}(\text{NO}_3)_2$ . Wind Pt wire around paper and ppt. and incinerate. A green mass is  $y\text{ZnO} \cdot x\text{CoO}$ .

#### NOTES

1.  $\text{NH}_4\text{Cl}$  is added, first, to prevent Mg from precipitating with the Third Group metals; second, because it aids in the precipitation and filtration of the sulphides by preventing them from going into the colloidal condition.

2. The solution is made alkaline with  $\text{NH}_3$  to neutralize the free acid. An excess of strong  $\text{NH}_4\text{OH}$  is then added to form with the  $\text{H}_2\text{S}$  the  $(\text{NH}_4)_2\text{S}$  which precipitates all the metals of this group. Treatment of the ammoniacal solution with  $\text{H}_2\text{S}$  is preferable to the use of  $(\text{NH}_4)_2\text{S}$ , for the reason that with the former  $\text{NiS}$  is prevented from going into solution. If, however,  $(\text{NH}_4)_2\text{S}$

is preferred, the filtrate from Group II. after the addition of 2 g. of  $\text{NH}_4\text{Cl}$  should be first rendered alkaline with  $(\text{NH}_4)\text{OH}$ , heated to boiling, and then treated with an excess of colorless  $(\text{NH}_4)_2\text{S}$ .

3. Vigorous stirring and heating of the precipitate will have the effect of rendering it more compact and easier to filter.

4. If the filtrate has a dark brown or black color, Ni is probably present.

5. The filtrate is at once acidified with acetic acid to destroy the excess of  $(\text{NH}_4)_2\text{S}$ , which, on standing, would oxidize to sulphate and precipitate the alkaline earths. Rendering the solution acid also prevents the formation of  $(\text{NH}_4)_2\text{CO}_3$  from the absorption of atmospheric  $\text{CO}_2$ .  $(\text{NH}_4)_2\text{CO}_3$ , if formed, would also precipitate the alkaline earths.

6. The  $\text{H}_2\text{S}$  is expelled because, like  $(\text{NH}_4)_2\text{S}$ , it is capable of being oxidized partially to  $\text{H}_2\text{SO}_4$  on exposure to air.

7. The residue obtained may consist of  $\text{NiS}$  (when  $(\text{NH}_4)_2\text{S}$  has been used as the precipitant) and coagulated S, and may be tested for Ni either with a borax bead in the O. F., or by solution of the ppt. in hot dil.  $\text{HNO}_3$ , rendering alkaline with  $\text{NH}_4\text{OH}$  and adding dimethylglyoxime.

8. The precipitate is rapidly filtered with the aid of a fluted filter in order to prevent the atmospheric oxidation of the sulphides to sulphates; for the same reason, it is recommended that the wash water contain a little  $(\text{NH}_4)_2\text{S}$ .  $\text{NH}_4\text{Cl}$  is added to the wash water to prevent the precipitate from passing through the filter in the colloidal condition. It is also well to keep the funnel covered as much as possible during the filtering and washing to minimize the oxidizing influence of the air.

9. The separation of Ni and Co from the remaining metals by the use of  $\text{HCl}$  (1 : 9) is not complete; small amounts of Ni and Co may pass into solution, while portions of  $\text{FeS}$  and other acid-soluble sulphides may be mechanically inclosed by S and thus escape solution by the acid.

10. A black residue does not prove the presence of Ni or Co for the reason stated in note 9; it may be  $\text{FeS}$  inclosed by S. It is also well to remember that metals of the Second Group, that have not been completely precipitated by  $\text{H}_2\text{S}$ , will appear at this point.

11. The experiments of Curtman and Rothberg show that in mixtures of the sulphides of Ni and Co containing as little as 3%  $\text{CoS}$ , a blue bead is obtained. With 2.5% of  $\text{CoS}$  uncertain results are obtained, while with 2% or less of  $\text{CoS}$ , the mixtures give brown beads.

12. Evaporation to 1 or 2 drops will suffice; if the evaporation is carried to the point of dryness, care must be taken not to ignite the residue. Should the residue be accidentally ignited, redissolve in hot *aqua regia* and evaporate again to a few drops.

13. These conditions must be closely adhered to.  $\text{KNO}_3$  precipitates Co best in a concentrated solution acid with acetic acid; no mineral acid is permissible, owing to the solubility of the precipitate therein. The free HCl is neutralized by the addition of NaOH in slight excess and the latter in turn is neutralized by acetic acid. Should a larger volume than 10 cc. be obtained in making the test, it is recommended that the solution be evaporated to 10 cc. before saturating with KCl.

14. Under the conditions stated in Note 13, complete precipitation of Co by  $\text{KNO}_3$  takes place after a lapse of 24 hours. By saturating the solution of Co with KCl, in which  $\text{K}_3\text{Co}(\text{NO}_3)_6$  is insoluble, and by using an excess of  $\text{KNO}_3$ , the precipitation of Co may be rendered complete in a half hour.

15. Not infrequently a precipitate of uncertain color is obtained with NaOH. In that case the presence of Ni cannot be considered proved until a characteristic Ni bead is obtained. It is however better to employ the dimethylglyoxime test which is more sensitive and characteristic for Ni.

16. The solution is evaporated to 1 cc. to remove the excess of HCl which, if present, would neutralize the NaOH next to be added. The  $\text{H}_2\text{S}$  is expelled at the same time.

17.  $\text{Na}_2\text{O}_2$  added to water even in the cold decomposes, giving  $\text{NaOH} + \text{O}$ . At higher temperatures the decomposition takes place violently.  $\text{Na}_2\text{O}_2$  should, therefore, be added in small portions to the cold solution with constant stirring; the final mixture, which should be strongly alkaline, must be boiled for a minute to decompose the excess of  $\text{Na}_2\text{O}_2$  and the perchromates which first form. The  $\text{Na}_2\text{O}_2$  furnishes the oxygen necessary for the oxidation of the chromite to chromate. It is important to remember that unless the solution is strongly alkaline, some Zn will be precipitated on boiling and diluting the mixture, due to the reversibility of the reaction, thus:—



18. Any Ni and Co dissolved by the 1.02 HCl will appear at this point; their presence, however, does not interfere with the tests for Fe and Mn.

19. A decidedly blue precipitate should be obtained if Fe is present. A blue coloration or a brown or white precipitate is not to be taken as proof of the presence of Fe. In making this test, care must be taken not to add more than a few drops of  $\text{K}_4\text{Fe}(\text{CN})_6$ , as the precipitate is soluble in an excess.

20. If the filtrate is yellow, Cr is present; if colorless, the test for Cr need not be made. A portion of this solution may be tested directly for Cr by acidifying with  $\text{HNO}_3$ , cooling thoroughly, adding 1 cc. each of ether and 3%  $\text{H}_2\text{O}_2$  and shaking. A blue color in the ether layer proves the presence of Cr.

21. The  $\text{NH}_4\text{Cl}$  is added to prevent a partial precipitation of Zn.

22. An excess of  $\text{NH}_4\text{OH}$  is to be avoided because of the slight solubility of  $\text{Al}(\text{OH})_3$  in excess.

23. The  $\text{Co}(\text{NO}_3)_2$  solution must be very dilute; if strong, it will, on ignition, yield black  $\text{CoO}$ , which will obscure the blue color of cobalt aluminate. The same applies to the confirmatory test for  $\text{Zn}$ .

24. It not infrequently happens that the solution contains sufficient sulphates to cause a precipitate of  $\text{BaSO}_4$  (white) to form along with the  $\text{BaCrO}_4$  (light yellow), thus obscuring the test for  $\text{Cr}$ ; hence the necessity of making the confirmatory test.

25. The addition of  $\text{NaC}_2\text{H}_5\text{O}_2$  represses the ionization of the acetic acid with the result that the solvent action of the latter on  $\text{BaCrO}_4$  is reduced to a minimum.

26. If the filtrate from the  $\text{BaCrO}_4$  is not clear, filter again, through another double filter, and repeat this treatment until a perfectly clear filtrate is obtained.

27. If a black ppt., due to  $\text{FeS}$ ,  $\text{NiS}$ , etc., is obtained, add dil.  $\text{HCl}$ , heat, and filter. Render filtrate alkaline with  $\text{NaOH}$ , add a little  $\text{Na}_2\text{O}_2$ , boil, dilute, and filter. Test filtrate with  $\text{H}_2\text{S}$ . A white ppt. is  $\text{ZnS}$ .

28. A slight precipitate of  $\text{Al}(\text{OH})_3$  is nearly always obtained, being derived from the reagents as well as from the action of  $\text{NaOH}$  on the glass. Judgment must therefore be exercised in reporting the presence of  $\text{Al}$  in the substance analyzed.

#### GROUP IV. THE ALKALINE EARTHS

The alkaline earth metals, barium, strontium, and calcium, are distinguished from the metals of the preceding group by the fact that their salts are neither precipitated by  $\text{H}_2\text{S}$  nor by  $(\text{NH}_4)_2\text{S}$ ; they are grouped together and are distinguished from Group V. by reason of their common property of being precipitated by  $(\text{NH}_4)_2\text{CO}_3$  in the presence of  $\text{NH}_4\text{Cl}$ .

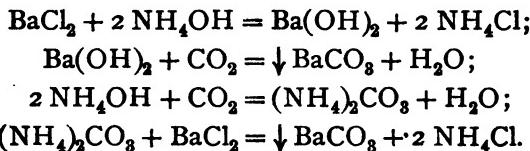
As the "analytical" grouping happens to be identical with their classification according to the Periodic Law, the order of variation in properties becomes an easy matter to remember; for, in most cases, the solubilities of the compounds of strontium are intermediate between those of barium and calcium. Unless the acid radical imparts a color, the salts of the alkaline earths are white or colorless, and, for the most part, insoluble in water.

The sulphides, like those of aluminum and chromium, can only exist in the dry state; when treated with water, they are at once hydrolyzed with the formation of the hydroxide and the evolution of  $\text{H}_2\text{S}$ .

### Reactions of the Salts of Barium

Many of the salts of barium are insoluble in water; excepting the sulphate and fluosilicate, all are, however, soluble in dilute hydrochloric acid.

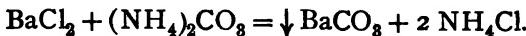
**1. Ammonium Hydroxide** (free from carbonate), when added to a solution of barium salts, does not yield a precipitate. If, however, the clear alkaline mixture is exposed to the air, or if ammonium hydroxide from the reagent bottle\* is used, a turbidity results from the formation of barium carbonate. The hydroxide is not precipitated because of its ready solubility in water (1 part in 20 of cold water):—



**2. Ammonium Sulphide** (free from carbonate) does not precipitate barium salts; on standing in the air, or with  $(\text{NH}_4)_2\text{S}$  from the reagent bottle, a slight turbidity results from the formation of barium carbonate. Reagent  $(\text{NH}_4)_2\text{S}$ , being an alkaline liquid, will, in consequence of absorption of atmospheric  $\text{CO}_2$ , contain a little  $(\text{NH}_4)_2\text{CO}_3$ , hence it will yield an immediate turbidity with barium salts:—

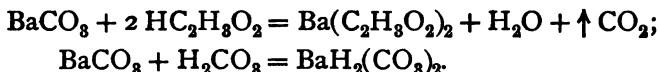
- (1)  $(\text{NH}_4)_2\text{S} + \text{BaCl}_2 = \text{BaS} + 2 \text{NH}_4\text{Cl};$
- (2)  $\text{BaS} + 2 \text{H}_2\text{O} = \text{Ba}(\text{OH})_2 + \uparrow \text{H}_2\text{S};$
- (3)  $\text{Ba}(\text{OH})_2 + \text{CO}_2 \downarrow \text{BaCO}_3 + \text{H}_2\text{O}.$

**3. Ammonium or Sodium Carbonate** produces in neutral or alkaline solutions of barium salts a white amorphous precipitate of  $\text{BaCO}_3$ , which, on standing or heating, becomes crystalline:—

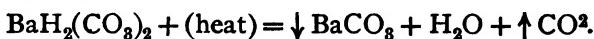


\* All alkaline liquids will, on exposure to the air, absorb  $\text{CO}_2$ , with the formation of carbonate proportional to the amount of  $\text{CO}_2$  absorbed; the reagent ammonium hydroxide will, therefore, always contain a little  $(\text{NH}_4)_2\text{CO}_3$ , and hence will yield a slight precipitate with the salts of the alkaline earths (see equations).

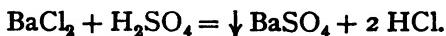
The precipitate is slightly soluble in  $\text{NH}_4\text{Cl}$ ; therefore, in very dilute solutions of barium salts containing much  $\text{NH}_4\text{Cl}$ , ammonium carbonate does not produce a precipitate. The precipitate is easily soluble in acids, even in acetic and carbonic acids:—



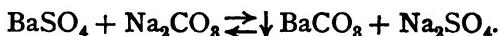
Boiling the dicarbonate decomposes it with the evolution of  $\text{CO}_2$  and precipitation of the normal carbonate:—



4. Dilute Sulphuric Acid or any soluble sulphate produces even in very dilute solutions of barium salts a heavy, white, finely divided precipitate of  $\text{BaSO}_4$ , practically insoluble in water (1 part in 400,000 parts of water):—



The precipitate is insoluble in alkalies, and is nearly insoluble in dilute but is somewhat soluble in strong acids. Boiled with a strong solution of  $\text{Na}_2\text{CO}_3$ , it undergoes partial decomposition, according to the equation:—

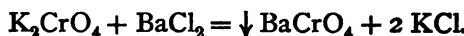


The decomposition is incomplete because of the reversibility of the reaction. If, however, the mixture is filtered, and the residue of  $\text{BaCO}_3$  and unchanged sulphate is boiled with a fresh  $\text{Na}_2\text{CO}_3$  solution, more  $\text{BaSO}_4$  will be converted to carbonate. By repeating this process a sufficient number of times, one can transform all the sulphate to carbonate. As the carbonate, after thorough washing, is easily soluble in acids, it will be seen that this procedure offers a means of getting an insoluble sulphate into solution.

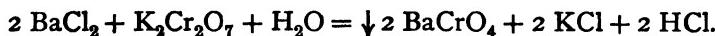
A better and more expeditious method of rendering the reaction complete consists in fusing the sulphate of barium with several times its weight of  $\text{Na}_2\text{CO}_3$ . Under these conditions, the reaction proceeds to completion in one operation. On cooling the melt, boiling it with water, and filtering, there will

remain on the filter a residue of  $\text{BaCO}_3$  equivalent in amount to the  $\text{BaSO}_4$  taken; the carbonate is then taken into solution with dilute hydrochloric acid. The method of *fusion with alkali carbonate* just outlined is of general application and is employed where it is desired to take into solution substances which are insoluble in water and in acids. The sulphates of strontium and calcium, though not as insoluble as that of barium, are sufficiently insoluble to be classed with insoluble substances and may be got into solution by the fusion method.  $\text{PbSO}_4$ ,  $\text{SrSO}_4$ , and  $\text{CaSO}_4$  may be completely converted into carbonate by the first method.

**5. Potassium Chromate** precipitates from neutral or acetic acid solutions yellow barium chromate :—



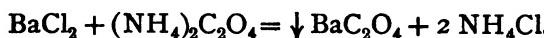
The precipitate is practically insoluble in water (1 part in 250,000) and in acetic acid (distinction from Sr and Ca), but is soluble in mineral acids. With potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) only partial precipitation results :—



This is due to the formation of HCl, which exerts a solvent action on  $\text{BaCrO}_4$ ; the addition of sodium acetate will render the precipitation complete.

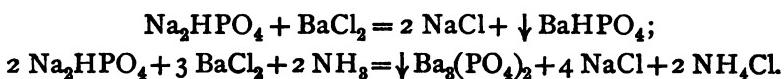
$\text{BaCrO}_4$ , like  $\text{BaSO}_4$ , is best precipitated in a boiling solution; for under these conditions the precipitate is obtained in a form which can be readily filtered and washed, without passing through the pores of the filter.

**6. Ammonium Oxalate** precipitates from moderately dilute solutions white barium oxalate, somewhat soluble in water (1 part in 2600) and completely soluble in boiling acetic acid (distinction from Ca):—



**7. Disodium Phosphate** precipitates in neutral solutions white flocculent  $\text{BaHPO}_4$ ; in ammoniacal solutions, sodium phos-

phate throws down the tertiary phosphate. The precipitates are easily soluble in dilute acids, even in acetic acid:—



**8. Flame Reaction.** Barium salts, preferably the chloride, when heated on a platinum wire in the bunsen flame, impart to it an apple-green color; frequently it is yellowish green, due to sodium as an impurity. The reaction becomes more delicate if the wire is first moistened with concentrated HCl.

### STRONTIUM

1. **Ammonium Hydroxide.** Same as with Ba salts.
2. **Ammonium Sulphide.** Same as with Ba salts.
3. **Ammonium Carbonate** precipitates white  $\text{SrCO}_3$ , more insoluble in water than  $\text{BaCO}_3$ ; in other respects, it possesses about the same solubilities as  $\text{BaCO}_3$ .
4. Dilute sulphuric acid or any soluble sulphate yields a white precipitate of  $\text{SrSO}_4$ . The precipitate is more soluble in water (1 part in 7000) and in acids than  $\text{BaSO}_4$ , and, as a consequence, is precipitated from very dilute solutions only after some time; it is, however, much less soluble in water than  $\text{CaSO}_4$ , the latter dissolving in water to the extent of 1 part in 500.  
 $\text{SrSO}_4$  is practically insoluble in a strong solution of  $(\text{NH}_4)_2\text{SO}_4$ , even on boiling (distinction and method of separation from Ca).
5. **Saturated  $\text{CaSO}_4$  Solution** yields with dilute solutions of strontium salts a precipitate of  $\text{SrSO}_4$ , which forms only after some time (distinction from Ba, which yields an immediate precipitate). Precipitation in this case, as well as in 4, is promoted by heating, and is retarded by the addition of acids. From concentrated solutions of Sr salts, an immediate precipitate is obtained.
6. **Potassium Chromate** does not yield a precipitate with dilute solutions of strontium salts or with concentrated solutions acid with acetic acid (distinction from and method of separation from

Ba). From neutral concentrated solutions, however, a yellow crystalline precipitate of  $\text{SrCrO}_4$  forms which is soluble in acetic acid.

7. **Ammonium Oxalate.** Same as with Ba.  $\text{SrC}_2\text{O}_4$  is only sparingly soluble in acetic acid.

8. **Disodium Phosphate.** Same as with Ba.

9. **Flame Reaction.** Strontium salts, preferably the chloride, when heated on a platinum wire in the bunsen flame, impart to it a deep red color.

### CALCIUM

1. **Ammonium Hydroxide.** Same as with Ba.

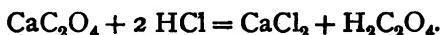
2. **Ammonium Sulphide.** Same as with Ba.

3. **Ammonium Carbonate** precipitates white amorphous  $\text{CaCO}_3$ , becoming crystalline on heating; it is more insoluble in water than  $\text{BaCO}_3$ , but in other respects its solubilities are about the same as those for  $\text{BaCO}_3$ .

4. **Dilute Sulphuric Acid** or any alkali sulphate does not produce a precipitate from dilute solutions. From concentrated solutions a white precipitate of  $\text{CaSO}_4$  is obtained which is appreciably soluble in a hot concentrated solution of  $(\text{NH}_4)_2\text{SO}_4$  (distinction and method of separation from Sr). A saturated solution of  $\text{CaSO}_4$ , of course, does not precipitate Ca salts (distinction from Sr and Ba).

5. **Potassium Chromate** does not yield a precipitate from dilute neutral solutions or from concentrated solutions acid with acetic acid.

6. **Ammonium Oxalate** produces a white crystalline precipitate of calcium oxalate immediately from strong solutions and slowly from dilute solutions of calcium salts. The presence of free ammonia, or heating, facilitates the precipitation. The precipitate is practically insoluble in water (1 part in 170,000) and in acetic acid, but is readily soluble in mineral acids:—



This is a most delicate test for Ca.

7. **Disodium Phosphate** gives the same reaction as with Ba.

8. **Flame Test.** Calcium salts, preferably the chloride, when heated on a platinum wire in the bunsen flame, impart to it a yellowish red color.

#### Outline of the Method of Analysis for Group IV

With certain mixtures it is possible, with a little practice, to detect all the metals of this group when occurring together by the simple flame reactions, as the characteristic colors do not all appear at the same time; the latter fact is due to the difference in the volatility of the chlorides. By an analysis of the flame colorations with the spectroscope it is not difficult to detect all the alkaline earths, even when they are all present together in the same solution. But as the spectroscopic and flame tests do not distinguish between significant amounts and mere traces due to accidental impurity, they cannot be relied on to determine the composition of an unknown substance. They are, however, exceedingly valuable as confirmatory tests and for the detection of traces. If the filtrate from Group III., concentrated to a few cc., fails to yield a flame coloration, the absence of Group IV. would be proved, although the reverse would not hold.

If the solution to be analyzed for Group IV. is the filtrate from Group III., it will contain a sufficient amount of  $\text{NH}_4\text{Cl}$  to prevent the precipitation of Mg along with the alkaline earth carbonates on adding the group reagent,  $(\text{NH}_4)_2\text{CO}_3$ . The precipitated carbonates are dissolved in acetic acid and from this diluted solution the barium is separated from the remaining metals of this group by precipitation with  $\text{K}_2\text{CrO}_4$ . After filtering the  $\text{BaCrO}_4$ , the filtrate will contain, besides Sr and Ca, an excess of  $\text{K}_2\text{Cr}_2\text{O}_7$ . By reprecipitating the Sr and Ca as carbonates, and filtering, they can be separated from the excess of chromate. If the carbonates are now dissolved in acetic acid, and the resulting solution is boiled with a solution of  $(\text{NH}_4)_2\text{SO}_4$  and filtered, the Sr will be on the filter as  $\text{SrSO}_4$ , while the Ca will pass into the filtrate. From the

latter the calcium may be precipitated as  $\text{CaC}_2\text{O}_4$  with  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ .

The separation of Sr and Ca by the use of a boiling solution of  $(\text{NH}_4)_2\text{SO}_4$  is not complete; some  $\text{CaSO}_4$  remains undissolved, while at the same time a small amount of  $\text{SrSO}_4$  goes into solution. The necessity for making confirmatory flame tests is therefore apparent.

#### **SCHEME IV**

The filtrate from Group III., which has been acidified with acetic acid, boiled, and filtered from the coagulated sulphur and  $\text{NiS}$ , as described under Scheme III., should be perfectly clear; if cloudy, it should be boiled again for a few minutes and repeatedly filtered through a double filter until a perfectly clear liquid is obtained; it should then be concentrated by evaporation to about 30 cc.\*

**Preliminary Test for Group IV.** To a small portion of the clear filtrate in a test tube add  $\text{NH}_4\text{OH}$  to alkaline reaction and then a slight excess of  $(\text{NH}_4)_2\text{CO}_3$ , and warm; a white ppt. proves the presence of Group IV. If no ppt. is obtained, the absence of more than traces (1) of the alkaline earths is indicated; in that case proceed to Scheme V.

If the preliminary test shows the presence of Group IV., the entire filtrate contained in a beaker is made alkaline with  $\text{NH}_4\text{OH}$  and is heated nearly to boiling;  $(\text{NH}_4)_2\text{CO}_3$  is then added in slight excess and the mixture is warmed (but not boiled) (2). The ppt. is allowed to settle and then filtered. The filtrate (3) should be received in a small beaker labelled Group V., covered, and reserved. The ppt. may consist of  $\text{BaCO}_3$ ,  $\text{SrCO}_3$ , and  $\text{CaCO}_3$ . Wash once with hot water and reject the washings. Dissolve the ppt. on the filter with the least amount of hot dilute acetic acid (4). Make the volume up to 40-50 cc. by dilution with water (5), heat to boiling, and, while boiling, add  $\text{K}_2\text{CrO}_4$  drop by drop till precipitation is complete. Allow the ppt. to settle and filter (using a double filter) by decantation. Finally, with the aid of hot water, bring the ppt. on the filter.

\* Any  $\text{NH}_4\text{Cl}$  which separates out during the evaporation should be filtered off and rejected. The removal of an unnecessarily large excess of ammonium salts at this point is a decided advantage, because it reduces the amount of material that must be removed by volatilization in the subsequent examination for Group V.

Residue is yellow  $\text{BaCrO}_4$ . Wash twice with hot water and reject washings. Confirm by dipping clean Pt wire (9) moistened with conc. HCl into ppt., and hold in flame. Do this repeatedly; a green coloration appearing after some time confirms the presence of Ba (10).

Filtrate (6) may contain Sr and Ca as acetates and  $\text{K}_2\text{Cr}_2\text{O}_7$ . To remove the latter, add  $\text{NH}_4\text{OH}$  to alkaline reaction and then  $(\text{NH}_4)_2\text{CO}_3$  till precipitation is complete; heat and filter. If no ppt. forms, the absence of more than traces of Sr and Ca is indicated. Residue is  $\text{SrCO}_3$  and  $\text{CaCO}_3$ . Reject filtrate. Wash ppt. with hot water until the washings are no longer yellow; reject washings. Dissolve ppt. on filter in the least amount of hot dil. acetic acid, and dilute the resulting solution with an equal volume of water.

**Preliminary Test for Sr (7).** Pour a *very small portion* of this solution into a test tube and add a little  $\text{CaSO}_4$  solution, heat to boiling, and allow to stand for a few minutes. (a) A slowly forming ppt. or cloudiness indicates the presence of Sr; proceed according to (a). (b) No ppt. or cloudiness proves the absence of Sr; proceed according to (b).

(a) If Sr is present, render the remainder of the solution alkaline with  $\text{NH}_4\text{OH}$ , add 5 cc. of  $(\text{NH}_4)_2\text{SO}_4$ , boil for a few minutes, and filter. Ppt. is  $\text{SrSO}_4$ . Wash with hot water and confirm by flame test (8). Test filtrate for Ca by adding  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . A white ppt. insol. in  $\text{HC}_2\text{H}_8\text{O}_2$  is  $\text{CaC}_2\text{O}_4$ . Confirm by flame test.

(b) Make solution alkaline with  $\text{NH}_4\text{OH}$  and add  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . A white ppt. insol. in acetic acid is  $\text{CaC}_2\text{O}_4$ . Confirm by flame test.

#### NOTES

**1. Tests for traces of alkaline earths.** If no precipitate is obtained with  $(\text{NH}_4)_2\text{CO}_3$ , treat a small portion of the solution with dilute  $\text{H}_2\text{SO}_4$ , boil, and allow to stand for some time. A white precipitate of  $\text{BaSO}_4$  proves the presence of Ba. Treat another small portion with ~~water~~ ~~alkaline~~, add  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , heat to boiling, and allow to stand; a cloudiness or white precipitate proves the presence of Ca. Traces of Sr are best tested for by means of the spectroscope.

**2.** The mixture must not be boiled, because at the boiling temperature  $(\text{NH}_4)_2\text{CO}_3$  is decomposed according to the equation —



The carbonates, which are first thrown down as an amorphous precipitate, are converted by heating and stirring into the crystalline form which can be readily filtered and washed.

3. To insure completeness of precipitation, add a little  $(\text{NH}_4)_2\text{CO}_3$  to the filtrate; if a precipitate forms, add it to the first; if no precipitate forms, precipitation was complete.

4. This is accomplished by placing a test tube under the stem of the funnel and pouring on the precipitate a hot mixture of 5-10 cc. of dilute acetic acid and an equal volume of water, allowing the acid to pass through the filter and pouring the same acid repeatedly through the filter till all the precipitate is dissolved.

5. A preliminary test with  $\text{K}_2\text{CrO}_4$  should be made on a *small portion* of this solution. If a precipitate is obtained, Ba is present and the entire solution should be treated with  $\text{K}_2\text{CrO}_4$  as described in the scheme. If no precipitate is obtained, Ba is absent: in that case the solution should *not* be treated with  $\text{K}_2\text{CrO}_4$  solution, but on a *small portion* make a preliminary test for Sr with  $\text{CaSO}_4$  solution; if present, treat the remainder of the solution according to (a); if absent, proceed to (b).

6.  $\text{BaCrO}_4$ , even when precipitated in a boiling solution, may pass through the filter, yielding a cloudy filtrate; when this is the case, the filtrate must be boiled again and refiltered.

7. It is important to use only a portion of the liquid for the preliminary test. If by mistake the entire filtrate is used, the test for Ca obviously cannot be made.

8. The confirmatory test for Sr is made by moistening the precipitate with concentrated HCl, dipping the wire into it and holding in the flame. A deep red coloration confirms the presence of Sr. If all the Ba had not been completely precipitated as chromate, it will appear here as white  $\text{BaSO}_4$ , but can readily be distinguished from  $\text{SrSO}_4$  by its failure to yield a red coloration to the flame.

9. A perfectly clean platinum wire must impart no color to the colorless bunsen flame. When this is not the case, an impurity is indicated, and this may be removed by one of the following methods:

(a) Any large particles of matter adhering to the wire must first be mechanically removed. The wire is then dipped into concentrated C.P. HCl, contained in a weighing or small specimen tube, and then held in the flame for several seconds. The acid dissolves and thus removes some of the adhering material and partly converts some of the still remaining impurity on the wire into chlorides which are volatilized in the flame. Repeat this operation several times; finally dip wire into *fresh* acid, and hold in flame. If clean, it should give no color to the flame.

*Under no circumstances must the wire, clean or otherwise, be dipped into the reagent bottle of acid.* The efficiency of this method will be indicated by the fact that the flame coloration becomes noticeably fainter with each treatment.

(b) Should the above treatment, however, fail to cleanse the wire, it must be dipped while red hot into borax, and heated until a bead forms. By properly manipulating the wire in the flame, the bead can be made to travel back and forth several times over the entire length of the wire. It is then shaken off. Should any solid material then adhere to the wire, it can now be readily removed by scouring with sand. The wire is then treated with concentrated HCl as described in (a).

10. The Pt wire need only be dipped *once* into the BaCrO<sub>4</sub> precipitate. After the first heating with HCl, it should be moistened with HCl again and heated. This is to be repeated several times without redipping into the BaCrO<sub>4</sub> precipitate.

## GROUP V

Group V. embraces the metal magnesium, the alkali metals potassium and sodium, and the metallic radical ammonium (NH<sub>4</sub>). Magnesium is closely allied from an analytical standpoint to the alkaline earths, for its hydroxide, carbonate, and phosphate are insoluble in water. It has been placed in Group V. for the reason that in the course of complete analysis it will be found in the last filtrate along with the alkali metals. This, of course, is due to the presence of NH<sub>4</sub>Cl in precipitating the third and fourth groups.

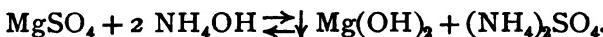
The test for NH<sub>4</sub> is not made on the final filtrate, because the latter will always contain ammonium salts added in the form of reagents in the regular course of analysis. The test, therefore, must always be made on a portion of the *original* substance. The other alkali metals, lithium, caesium, and rubidium, belong to this group, but have not been included because of their rare occurrence.

Omitting consideration of magnesium, which serves as a bridge between groups IV. and V., it may be stated that the chief characteristic of the alkali metals is the fact that *nearly all their salts are soluble in water*; thus, the chloride, sulphate, sulphide, nitrate, phosphate, oxalate, carbonate, and hydroxide are soluble in water; indeed, their aqueous solutions have been used as reagents. Excluding NH<sub>4</sub>, all the alkali metals give characteristic flame and spectroscopic reactions.

### MAGNESIUM

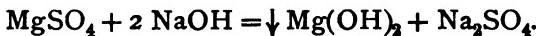
Magnesium salts are colorless. With the exception of the hydroxide, carbonate, phosphate, arsenate, and arsenite, all the salts of magnesium are soluble in water. They do not color the bunsen flame. Neither  $\text{NH}_4\text{OH}$ ,  $(\text{NH}_4)_2\text{S}$ , nor  $(\text{NH}_4)_2\text{CO}_3$  precipitates magnesium salts in the presence of a sufficient amount of ammonium chloride, hence the classification of magnesium with the alkali metals.

1. **Ammonium Hydroxide** gives a partial precipitation of gelatinous magnesium hydroxide,  $\text{Mg}(\text{OH})_2$ , readily soluble in ammonium salts :—



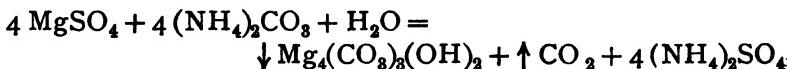
The precipitation is only partial in consequence of the formation of an ammonium salt as a by-product of the reaction. The precipitate is readily soluble in acids. The solubility of the precipitate in  $\text{NH}_4$  salts, or, what amounts to the same thing, the non-precipitation of Mg salts by  $\text{NH}_4\text{OH}$  in the presence of a sufficient amount of  $\text{NH}_4$  salts, is a phenomenon of the same order as that already met with in the cases of ferrous, manganese, and zinc compounds.

2. **Sodium, Potassium, or Calcium Hydroxide** completely precipitates, in the absence of  $\text{NH}_4$  salts,  $\text{Mg}(\text{OH})_2$ , insoluble in excess and nearly insoluble in water, the solubility being 1 part in 10,000. The washed precipitate is soluble in  $\text{NH}_4$  salts :—

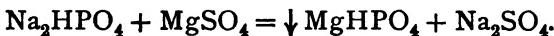


Boiling promotes precipitation.

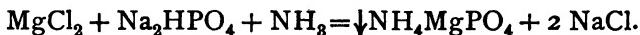
3. **Ammonium Carbonate**, in the presence of  $\text{NH}_4$  salts, gives no precipitate. In solutions containing no  $\text{NH}_4$  salts, a white basic salt precipitates on standing or on boiling. The composition of the precipitate is variable, depending upon the conditions of concentration and temperature :—



4. **Disodium Phosphate**, when added to a neutral solution of a Mg salt, precipitates flocculent  $MgHPO_4$  :—



If, however,  $NH_4Cl$  and ammonia are added to the solution of a Mg salt before adding the sodium phosphate, a characteristic white crystalline precipitate of ammonium magnesium phosphate forms :—



From dilute solutions the precipitate forms slowly, but it may be hastened by cooling and vigorously stirring the mixture. The precipitate is slightly soluble in water (1 part in 13,500 at  $23^\circ C.$ ), but is practically insoluble in 2.5 per cent. ammonia water. It is readily soluble in acetic acid. The addition of  $NH_4Cl$  prevents the formation of the hydroxide when ammonium hydroxide is added. This is a most delicate test for Mg.

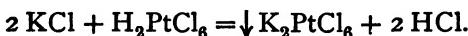
5. **Ammonium Oxalate** gives with dilute solutions of magnesium salts no precipitate ; from concentrated solutions, however, it yields a white precipitate of  $MgC_2O_4$ . The presence of  $NH_4$  salts renders the precipitation incomplete.

6.  $H_2S$ ,  $(NH_4)_2S$ , and  $H_2SO_4$  do not precipitate magnesium salts.

### POTASSIUM

With the exception of the acid tartrate, cobaltic nitrite, chloroplatinate, and perchlorate, nearly all the salts of potassium are soluble.

1. **Hydrochlorplatinic Acid** ( $H_2PtCl_6$ ) produces in neutral or in concentrated acid solutions of potassium salts a yellow crystalline precipitate of potassium chlorplatinate ( $K_2PtCl_6$ ) :—



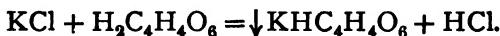
From moderately dilute solutions the precipitate separates out only after standing, but may be hastened by cooling, stirring, or shaking the mixture vigorously in a test tube. This applies to nearly all crystalline precipitates. The precipitate is soluble in

alkalies ; it dissolves in water to the extent of 1 part in 100 at 15° C. It is practically insoluble in 80 per cent. alcohol. On ignition it decomposes according to the following equation :—

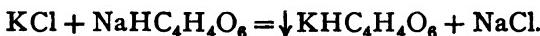


Solutions of potassium iodide and potassium cyanide do not give this precipitate ; they should first be changed to chloride by evaporation with concentrated HCl. As NH<sub>4</sub> salts yield a similar precipitate they must be removed before the test is applied.

2. **Tartaric Acid** (H<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>) produces in neutral solutions of potassium salts, which are moderately concentrated, a white crystalline precipitate of potassium acid tartrate :—



Precipitation may be hastened by vigorously shaking the mixture. The precipitate is soluble in alkalies and in mineral acids. A solution of sodium acid tartrate (NaHC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>) is preferable, as it does not yield any free acid as a by-product :—



The solubility of the precipitate in water at 15° C. is 1 part in 222. The reaction is a little more than twice as sensitive as 1. Ammonium salts must be absent as they yield a similar precipitate with the reagent.

3. **Sodium Cobaltic Nitrite** [Na<sub>3</sub>Co(NO<sub>2</sub>)<sub>6</sub>] yields, with solutions of potassium salts acidified with acetic acid, a yellow precipitate of potassium cobaltic nitrite [K<sub>3</sub>Co(NO<sub>2</sub>)<sub>6</sub>]. From dilute solutions the precipitation may be hastened by warming the mixture. The precipitate is soluble in water to the extent of 1 part in 11,000 at 15° C. and is therefore the most sensitive of the reactions mentioned. The test cannot be applied in the presence of NH<sub>4</sub> salts for the reason that the latter yield a similar precipitate.

4. **Flame Reaction.** Potassium salts, preferably the chloride and nitrate, when heated on a platinum wire in the bunsen flame, impart to it a violet color. The sensitiveness of this reaction was given by Bunsen to be 0.001 mg. KCl. The presence

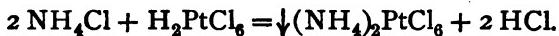
of even small amounts of sodium compounds interferes with this reaction by masking the color. If, however, the flame is viewed through several thicknesses of cobalt glass, the latter will absorb the yellow rays and thus permit the violet color to be seen.

5. When heated just below a red heat, potassium chloride is not volatilized (distinction from  $\text{NH}_4$  salts).

### AMMONIUM

The ammonium salts very closely resemble the potassium compounds. They have the same crystalline form and, in general, about the same solubility.

1. **Hydrochlorplatinic Acid** ( $\text{H}_2\text{PtCl}_6$ ) precipitates, under the same conditions given for potassium compounds (which see), a yellow crystalline precipitate of ammonium chlorplatinate,  $(\text{NH}_4)_2\text{PtCl}_6$  :—



The precipitate may easily be distinguished from the corresponding potassium compound by the fact that it is decomposed by an excess of NaOH with the evolution of  $\text{NH}_3$  :—



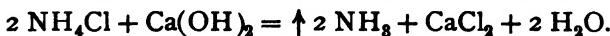
When strongly heated, it leaves a residue of platinum sponge *only* (distinction from the K compound). Ammonium chlorplatinate is somewhat less soluble in water than the corresponding K compound; it is insoluble in alcohol.

2. **Sodium Cobaltic Nitrite** yields with solutions of ammonium salts a yellow precipitate similar to that given by potassium salts. Hence before testing for potassium with this reagent, all the ammonium salts must be removed.

3. **Tartaric Acid** ( $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ ) or  $\text{NaHC}_4\text{H}_4\text{O}_6$  gives from concentrated solutions of ammonium salts a crystalline precipitate of  $\text{NH}_4\text{HC}_4\text{H}_4\text{O}_6$ . The precipitate is soluble in acids and in alkalies, and is very much more soluble in water than the corresponding K compound; for this reason it is not a good test.

It may be distinguished from the corresponding K compound by the evolution of NH<sub>3</sub> when treated with an excess of NaOH.

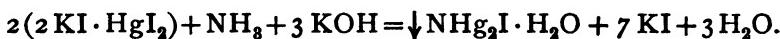
**4. Sodium Hydroxide.** All ammonium compounds, when heated with an excess of caustic soda, potash, or lime, undergo decomposition with the evolution of ammonia gas; the latter may be detected by its characteristic odor or by the ability of the gas evolved to turn moistened red litmus paper blue:—



The evolved NH<sub>3</sub> may be further recognized by holding in the escaping vapor a piece of filter paper moistened with mercurous nitrate solution. Ammonia, if present, will blacken the paper in accordance with the following reaction:—



**5.** For the detection of minute amounts of ammonia, such, for instance, as are present in drinking water, an alkaline solution of mercuric potassium iodide, known as Nessler's reagent, is used. With this solution, a yellow coloration is obtained which deepens in color, becoming brown with relatively greater amounts. With still greater amounts a brown precipitate is obtained.



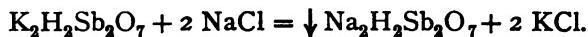
**6.** All ammonium salts are volatilized at a temperature just below a red heat (distinction and method of separation from Na and K salts), some undergoing decomposition at the same time.

### SODIUM

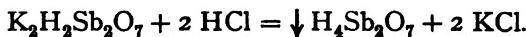
All of the salts of sodium, with the exception of the pyroantimonate, are soluble in water.

**1. Potassium Pyroantimonate Solution** (K<sub>4</sub>H<sub>2</sub>Sb<sub>2</sub>O<sub>7</sub>) precipitates from neutral or slightly alkaline solutions of sodium salts that are fairly concentrated, a white crystalline precipitate of sodium pyroantimonate (Na<sub>2</sub>H<sub>2</sub>Sb<sub>2</sub>O<sub>7</sub>). Precipitation may be

hastened by shaking the mixture vigorously in a test tube. Sodium pyroantimonate is soluble in boiling water to the extent of 1 part in 300:—



The solution must not be acid, for then decomposition of the reagent results with the precipitation of amorphous pyroantimonic acid:—



All other metals, with the exception of K and NH<sub>4</sub>, must be removed, for they too yield precipitates with the reagent.

2. Hydrochloroplatinic Acid, and Tartaric Acid, do not precipitate sodium salts.

3. Sodium Cobaltic Nitrite does not give a precipitate with sodium salts (distinction from K and NH<sub>4</sub>).

4. Heated just below a red heat, sodium compounds are not volatilized (distinction from NH<sub>4</sub>).

5. Flame Reaction.—Sodium compounds color the bunsen flame yellow even when the quantity is very small. Bunsen and Kirchhoff state that as small an amount as  $\frac{1}{300000}$  of a milligram of sodium will give a flame test. To distinguish between a trace and a significant amount, attention must be given to the intensity and duration of the coloration.

#### Outline of the Method of Analysis for Group V

As the special tests for most of the metals of Group V. are not interfered with by the presence of the others, it is needless in most cases to effect their separation before applying the test; thus, the precipitation test for potassium may be made in the presence of sodium, and the test for Mg may be made in the presence of all the alkali metals, for the latter are not precipitated by Na<sub>2</sub>HPO<sub>4</sub>. The test for Mg is therefore carried out on a small portion of about one-third of the filtrate from Group IV. It must, however, be remembered that Na<sub>2</sub>HPO<sub>4</sub> precipitates the alkaline earth metals; and as the latter are usually present

in small amounts in the last filtrate by reason of the slight solubility of their carbonates in  $\text{NH}_4\text{Cl}$ , they must first be removed before the test can be applied. This is accomplished by adding a little  $(\text{NH}_4)_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , boiling, and filtering off the precipitated alkaline earths in the form of sulphates and oxalates. The filtrate, after concentration, may then be tested for magnesium.

The remaining two-thirds of the original filtrate is used for the detection of Na and K. As this filtrate contains a large amount of ammonium salts accumulated in the course of the analysis, and as the latter interfere with the precipitation tests for K by yielding similar precipitates, it is necessary to remove them before the test for K is made. This is accomplished by taking advantage of the fact that at a temperature just below a red heat, all  $\text{NH}_4$  salts are volatilized. The  $\text{NH}_4$  salts removed, the residue is moistened with a little water, and the flame tests are applied. If an intense yellow coloration is obtained which persists for some time, the presence of Na is proved; the flame may then be further examined for potassium by viewing it through several thicknesses of cobalt glass. If a violet-colored flame is obtained in the first place, Na is absent. In either case, a confirmatory test for potassium should be made by any one of the precipitation tests.

Ammonium is not tested for in this group for the previously mentioned reason that  $\text{NH}_4$  compounds in the form of reagents have been added to the solution in the course of the analysis. The test, which consists in liberating  $\text{NH}_3$  by heating with an excess of  $\text{NaOH}$ , must, therefore, always be made on a separate portion of the original substance.

## SCHEME V

## Analysis of the Filtrate from Group IV

This will contain, besides Mg and the alkalies, traces of the alkaline earths which were dissolved by  $\text{NH}_4\text{Cl}$ . Divide into two unequal portions.

In  $\frac{1}{2}$  test for Mg. Add a few drops of  $(\text{NH}_4)_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , boil and filter. Reject any ppt. which may form (1). Concentrate the filtrate by evap. to 5 cc. (should any ammonium salts crystallize out, filter and reject). To filtrate contained in a test tube add  $\text{NH}_4\text{OH}$  to alkaline reaction and then add  $\text{Na}_2\text{HPO}_4$ . Shake vigorously and allow to stand several minutes. A white cryst. ppt. which is soluble in acetic acid is  $\text{NH}_4\text{MgPO}_4$ .

In  $\frac{1}{2}$  test for Na and K. Evap. in a large evap. dish, if the vol. of the solution is large, to about 15 cc. Transfer to a small dish and continue to evap. over a wire gauze until sputtering occurs; then cover dish with a watch glass and gently heat until the mass is perfectly dry. By means of a glass rod, transfer to dish particles of salt adhering to the watch glass, place *uncovered* dish on a pipestem triangle, and ignite (under hood) until no more fumes of  $\text{NH}_4\text{Cl}$  (2) is given off, being careful to keep the dish *below* a red heat and to heat the sides and rim as well as the bottom of the dish. With the aid of a glass rod scrape any salt adhering to the sides of the dish into the center, and stir up salt at the bottom as much as possible; ignite again until no more  $\text{NH}_4\text{Cl}$  (2) is given off. Cool. Transfer a *small portion* of the residue to a watch glass, moisten with a drop of HCl, dip clean Pt wire into it, and hold in flame. A violet coloration proves the presence of K and absence of Na. An intense yellow coloration (3) which persists for some time proves the presence of Na; in that case, examine flame for K either with several thicknesses of cobalt glass or better with a spectroscope (4).

**Test for K.** The remainder of the residue in the dish is dissolved in the least amt. of hot water (3 cc.) just acidified with acetic acid, and is filtered through a small filter. To filtrate in a test tube add 1 cc. of  $\text{Na}_2\text{Co}(\text{NO}_2)_6$ , warm, and allow to stand for several minutes. A yellow ppt. confirms the presence of K.

**Test for  $\text{NH}_4$ .** This test is always made on a small portion of the original substance and never on the filtrate from Groups III. and IV. To about 5 cc. of the *original* solution or 0.2 – 0.5 g. of the original solid substance contained in a small beaker, add NaOH till the resulting mixture, after thorough stirring, is decidedly alkaline. Heat with stirring (5). Ammonia, if present, will be made evident by its characteristic odor and by its ability to turn blue a piece of red litmus paper held above the beaker.

## NOTES ON SCHEME V

1.  $\text{Na}_2\text{HPO}_4$  precipitates all the metals except the alkalies and As, so that the test for Mg can only be made in the absence of these metals. A flocculent precipitate of  $\text{AlPO}_4$  sometimes separates on adding  $\text{Na}_2\text{HPO}_4$ , but the latter is easily distinguished from  $\text{NH}_4\text{MgPO}_4$  by reason of its insolubility in acetic acid. In concentrating the solution to 5 cc.,  $\text{Al}(\text{OH})_3$  may separate out; in that case, it should be filtered off before adding the  $\text{Na}_2\text{HPO}_4$ .

Should a precipitate of doubtful form be obtained with  $\text{Na}_2\text{HPO}_4$  and it is desired to confirm the presence of Mg, the precipitate on the filter should be treated with a little acetic acid, the resulting clear filtrate made alkaline with  $\text{NH}_4\text{OH}$ , vigorously shaken, and allowed to stand for several minutes. If Mg is present, a white crystalline precipitate will form.

It is not customary to remove the Mg before testing for the alkalies. Should it be desired, however, to estimate the amount of K and Na, the Mg may be removed by first expelling  $\text{NH}_4$  salts by evaporation of the solution to dryness and thoroughly igniting the residue. The latter is then dissolved in water and the Mg is precipitated with  $\text{Ba}(\text{OH})_2$  solution, filtered, and the Ba in the filtrate removed by precipitation with sulphuric acid, or with  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{CO}_3$ .

2. Unless the last traces of  $\text{NH}_4$  salts are removed, the precipitation test for K will be worthless for the reason that  $\text{NH}_4$  salts yield a similar precipitate. During ignition, the bottom of the dish must not be allowed to reach a red heat because there will be danger of volatilizing  $\text{NaCl}$  and  $\text{KCl}$ . A small amount of black carbonaceous matter (due to carbonization of small quantities of pyridine which is usually present in the  $\text{NH}_4\text{OH}$ ) is left behind along with the chlorides of K and Na. This is, however, removed later when the residue is treated with water and filtered before making the precipitation test for K.

3. A fleeting yellow coloration is not to be taken as evidence of the presence of Na. The coloration should persist for at least 6 seconds.

4. The test for K should be confirmed always by a precipitation test.

5. Stirring the mixture while heating is important because of the tendency of the mixture to bump and the consequent danger of having the strongly alkaline mixture spurted into the eyes. Care should be taken in heating and stirring to prevent any of the alkaline liquid from coming in contact with the litmus paper. Failure to observe this precaution will vitiate the test.

If the original material is a solid instead of a solution, it is not necessary to get it into solution in order to test for  $\text{NH}_4$ . To a portion of the solid substance in a beaker, add  $\text{NaOH}$  in slight excess, forming a paste, and heat gently with stirring. The odor of  $\text{NH}_3$  evolved will prove the presence of  $\text{NH}_4$  compounds.

## ANALYSIS OF UNKNOWN SOLUTIONS FOR ALL GROUPS

To 25 cc. of solution add HCl and filter.

Residue : AgCl, PbCl <sub>2</sub> , HgCl. Analyze ac- cording to Scheme I.	Filtrate contains Groups II.-V. Bring to proper conditions of acidity and pass in H <sub>2</sub> S. Filter.
Residue : HgS, PbS, Bi <sub>2</sub> S <sub>3</sub> , CuS, CdS, As <sub>2</sub> S <sub>3</sub> , Sb <sub>2</sub> S <sub>3</sub> , SnS. Wash and treat with (NH <sub>4</sub> ) <sub>2</sub> S <sub>x</sub> . Filter. Analyze residue ac- cording to Scheme II..A. Analyze filtrate ac- cording to Scheme II. B.	Filtrate : Boil to expel H <sub>2</sub> S before proceeding with the analysis of Group II. ppt. Add NH <sub>4</sub> Cl, make alkaline with NH <sub>4</sub> OH, and completely ppt. with H <sub>2</sub> S or (NH <sub>4</sub> ) <sub>2</sub> S ; filter.
Residue : Al(OH) <sub>3</sub> , Cr(OH) <sub>3</sub> , FeS, NiS, CoS, MnS, ZnS. Analyze ac- cording to Scheme III.	Filtrate is at once acidified with acetic acid and boiled to expel H <sub>2</sub> S, and then filtered. Make clear filtrate alkaline with NH <sub>4</sub> OH, add (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> , and filter.
Residue : BaCO <sub>3</sub> , SrCO <sub>3</sub> , + CaCO <sub>3</sub> . Analyze ac- cording to Scheme IV.	Filtrate will contain Mg and the "alkalies." Divide into two portions : ½ test for Mg according to Scheme V; ½ test for Na and K according to Scheme V.

Test for NH<sub>4</sub> is made on a separate portion according to Scheme V.



## PART II

### THE ACIDS

It is customary to arrange the acids into groups according to their deportment with two reagents, viz.,  $\text{BaCl}_2$  and  $\text{AgNO}_3$ . Three groups are thus distinguished.

**Group I.** includes those acids whose barium or calcium salts are insoluble in water; they are therefore precipitated from neutral solutions by  $\text{BaCl}_2$ . This group is divided into two parts, namely: (a) Acids precipitated by  $\text{BaCl}_2$  from solutions acid with HCl, viz., sulphuric acid ( $\text{H}_2\text{SO}_4$ ) and hydrofluosilicic acid ( $\text{H}_2\text{SiF}_6$ ); (b) Acids precipitated by  $\text{BaCl}_2$  from neutral solutions only, viz., carbonic acid ( $\text{H}_2\text{CO}_3$ ), sulphurous acid ( $\text{H}_2\text{SO}_3$ ), thiosulphuric acid ( $\text{H}_2\text{S}_2\text{O}_3$ ), phosphoric acid ( $\text{H}_3\text{PO}_4$ ), hydrofluoric acid (HF), oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ), boric acid ( $\text{H}_3\text{BO}_3$ ),<sup>\*</sup> silicic acid ( $\text{H}_2\text{SiO}_3$ ),† tartaric acid ( $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ ), arsenic acid ( $\text{H}_3\text{AsO}_4$ ), arsenious acid ( $\text{H}_3\text{AsO}_3$ ), and chromic acid ( $\text{H}_2\text{CrO}_4$ ).

**Group II.** includes those acids whose barium salts are soluble in water, but whose silver salts are insoluble in nitric acid; they are therefore precipitated by  $\text{AgNO}_3$  from solutions acid with nitric acid. These acids follow:—

Hydrochloric acid (HCl), hydrobromic acid (HBr), hydriodic acid (HI), hydrocyanic acid (HCN), hydrogen sulphide ( $\text{H}_2\text{S}$ ), hydroferrocyanic acid [ $\text{H}_4\text{Fe}(\text{CN})_6$ ], hydroferricyanic acid [ $\text{H}_8\text{Fe}(\text{CN})_6$ ], thiocyanic acid (HSCN), and nitrous acid ( $\text{HNO}_2$ ); the last is, however, only precipitated from moderately

\* Orthoboric acid ( $\text{H}_3\text{BO}_3$ ) is here considered as representative of the acids of boron.

† Metasilicic acid ( $\text{H}_2\text{SiO}_3$ ) is taken as the type of the many silicic acids.

concentrated solutions and is therefore also placed in the next group.

**Group III.** includes those acids that are not precipitated by either  $\text{BaCl}_2$  or  $\text{AgNO}_3$ , viz., nitric acid ( $\text{HNO}_3$ ), nitrous acid ( $\text{HNO}_2$ ), chloric acid ( $\text{HClO}_3$ ), and acetic acid ( $\text{HC}_2\text{H}_3\text{O}_2$ ).

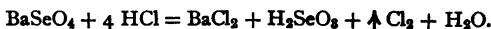
### SULPHATES

With the exception of the sulphates of lead, barium, strontium, and calcium, all normal sulphates are soluble in water. Silver and mercury (-ous) sulphates are, however, difficultly soluble. Nearly all basic sulphates are insoluble, but readily dissolve in hydrochloric or nitric acids. Alkali and alkaline earth sulphates are not decomposed when ignited gently in a closed tube, but at higher temperatures more or less decomposition takes place. The behavior of other sulphates on being heated varies with the nature of the metal with which the  $\text{SO}_4$  radical is united, some resisting decomposition, while others are readily decomposed, giving off  $\text{SO}_3$  or  $\text{SO}_2$ , or both, and leaving the oxide of the metal.

Free sulphuric acid is recognized even in the presence of a sulphate by its property, when concentrated, of removing the elements of water from organic substances and leaving a charred residue; thus, if to a solution containing free  $\text{H}_2\text{SO}_4$  a little cane sugar is added and the mixture is evaporated just to dryness, preferably on a steam bath, a black residue will be obtained.

**i.** **Barium Chloride** precipitates white  $\text{BaSO}_4$ ,\* insoluble in water and in dilute acids even on boiling. From dilute solutions a precipitate separates only on standing. Dilute  $\text{HCl}$  or  $\text{HNO}_3$

\* From  $\text{HCl}$  solutions  $\text{BaCl}_2$  may also precipitate  $\text{BaSeO}_4$  and  $\text{BaSiF}_6$ ; the former is readily distinguished from  $\text{BaSO}_4$  and  $\text{BaSiF}_6$  by the fact that on boiling it with concentrated  $\text{HCl}$ , chlorine is given off:—



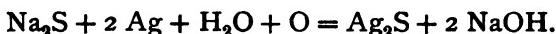
$\text{BaSiF}_6$  is easily recognized by its readiness to undergo decomposition when heated with concentrated  $\text{H}_2\text{SO}_4$ :—



should be added before the reagent in order to prevent the precipitation of chromates, sulphites, and carbonates. Strong acid must not be used, for otherwise a crystalline precipitate of  $\text{BaCl}_2$  or  $\text{Ba}(\text{NO}_3)_2$  may be obtained; these are, however, easily distinguished from  $\text{BaSO}_4$  by their ready solution on diluting. For further properties of  $\text{BaSO}_4$ , see reaction 4 under *Barium*.

2. **Lead Acetate** produces a white precipitate of  $\text{PbSO}_4$ , soluble in a hot concentrated solution of ammonium acetate or tartrate.

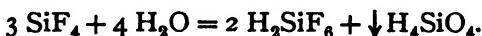
3. Mixed with  $\text{Na}_2\text{CO}_3$  free from sulphur compounds, and heated on charcoal with the reducing flame of a blowpipe, all sulphates are reduced to sulphides. If the fused mass is placed on a silver coin and then moistened with a drop of water, a black stain of  $\text{Ag}_2\text{S}$  will be produced:—



This test is also given by other sulphur compounds.

#### FLUOSILICATES

Hydrofluosilicic acid ( $\text{H}_2\text{SiF}_6$ ) is formed by the action of silicon tetrafluoride ( $\text{SiF}_4$ ) on water:—



If the silicic acid, which is formed at the same time, is filtered off, the filtrate will contain an aqueous solution of hydrofluosilicic acid. Both the acid and its salts are decomposed on heating. On evaporating a solution of  $\text{H}_2\text{SiF}_6$ , decomposition sets in, according to the equation—



With the exception of the potassium and barium salts, nearly all fluosilicates are soluble in water.

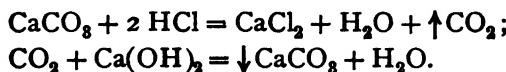
$\text{BaSiF}_6$ , formed by adding  $\text{BaCl}_2$  to a solution of a fluosilicate, is a white, crystalline, insoluble substance. Its solubility at  $17^\circ \text{C}$ . is 1 part in 3700 parts of water. As it is sparingly soluble in  $\text{HCl}$ , it can be precipitated by  $\text{BaCl}_2$  from solutions containing this acid. For a method of distinguishing it from  $\text{BaSO}_4$ , see footnote, page 124.

### CARBONATES

Carbonic acid ( $H_2CO_3$ ) is a weak dibasic acid which is only known in solution. With bases it yields an important class of stable salts known as carbonates. On ignition, the carbonates of calcium and strontium are decomposed, while the normal alkali carbonates are but slightly affected; ammonium carbonate volatilizes on heating. Nearly all of the carbonates are white, and, with the exception of the carbonates of the alkali metals, all the normal salts are insoluble in water. The aqueous solutions of the carbonates and dicarbonates of the alkalies possess an alkaline reaction. Sodium dicarbonate, on ignition, is changed to the normal salt with evolution of carbon dioxide and water :—



1. All the acids, excepting HCN, decompose carbonates with effervescence, due to the evolution of  $CO_2$ ; the latter may be recognized by its property of rendering turbid a drop of lime-water held in the escaping gas :—



This constitutes the chief reaction for carbonates from an analytical standpoint.

2. Barium or Calcium Chloride, when added to a solution of a normal carbonate, gives a white precipitate of  $BaCO_3$  or  $CaCO_3$ . The precipitate is soluble in carbonic acid as well as in all other acids with the exception of HCN :—



From the solution of dicarbonate of calcium,  $CaCO_3$  reprecipitates on boiling :—



3. Silver Nitrate precipitates white silver carbonate ( $Ag_2CO_3$ ), which, on boiling, changes to brown silver oxide ( $Ag_2O$ ) :—



## SULPHITES

The aqueous solution of sulphur dioxide, known as sulphurous acid, is a weak dibasic acid. When boiled it decomposes, giving off  $\text{SO}_2$ , which may be easily recognized by its odor. Neutralized by bases, it forms sulphites, all of which are insoluble or nearly so in water, with the exception of those of the alkali metals. The solid salts, as well as their aqueous solutions, readily oxidize on exposure to air, forming the corresponding sulphates.

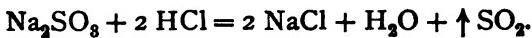
1. **Barium Chloride** precipitates from *neutral* solutions white barium sulphite ( $\text{BaSO}_3$ ), readily soluble in  $\text{HCl}$  and  $\text{HNO}_3$ . In practice, a residue of  $\text{BaSO}_4$  remains, due to the presence of a small amount of sulphate originally present in the sulphite or produced by the subsequent oxidation of the sulphite. If the  $\text{BaSO}_4$  is filtered off, the clear filtrate may be shown to contain sulphurous acid by adding a little bromine or concentrated  $\text{HNO}_3$  and boiling, when a white precipitate of  $\text{BaSO}_4$  will form. The bromine or nitric acid oxidizes the sulphurous to sulphuric acid, and the latter at once yields with the  $\text{BaCl}_2$  present a precipitate of  $\text{BaSO}_4$ .

Free sulphurous acid is not precipitated by  $\text{BaCl}_2$ .

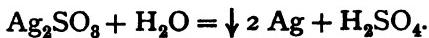
2. **Hydrogen Sulphide**, when passed into a solution of sulphurous acid, or a solution of a sulphite, acid with  $\text{HCl}$ , causes a separation of sulphur with the formation at the same time of pentathionic acid :—



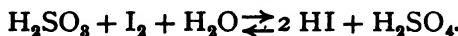
3. **Dilute  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$** , when added to a sulphite, decomposes it with the evolution of  $\text{SO}_2$  :—



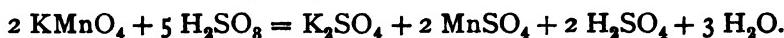
4. **Silver Nitrate** precipitates from neutral solutions white  $\text{Ag}_2\text{SO}_3$ , which, on boiling, is decomposed, with the separation of gray metallic silver :—



5. **Iodine Solutions** are bleached by sulphurous acid; this is due to the reduction of iodide to hydriodic acid :—

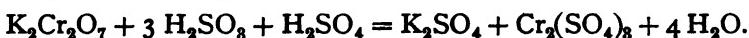


6. **Potassium Permanganate** solution, acid with sulphuric acid, is also decolorized by sulphurous acid :—

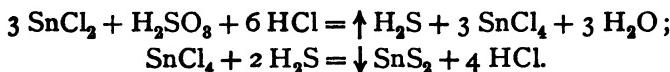


Since sulphur dioxide, which may be liberated from a sulphite (see reaction 3), is much heavier than air, it may be decanted into another test tube containing a small amount of exceedingly dilute  $\text{KMnO}_4$  solution. Now, on thoroughly mixing the gas and permanganate solution, the latter will be bleached.

7. **Potassium Dichromate**, when added to sulphurous acid, is reduced to a chromic salt; the reduction is accompanied by a change in color to green :—



8. **Stannous Chloride**, when added to sulphurous acid or to a hydrochloric acid solution of a sulphite, and the mixture heated, reduces the sulphurous acid to  $\text{H}_2\text{S}$ , which, after some time, will precipitate the tin as stannic sulphide :—



9. Sulphurous acid reduces arsenic acid ( $\text{H}_3\text{AsO}_4$ ) to arsenious acid ( $\text{H}_3\text{AsO}_3$ ); the action is preferably conducted in a closed pressure bottle heated in a water bath. It also reduces ferric to ferrous salts.

10. Sulphites, when heated with sodium carbonate on charcoal, behave in the same way as sulphates (see reaction 3).

### THIOSULPHATES

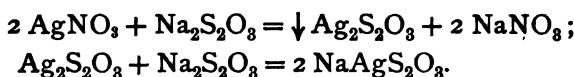
Thiosulphuric acid is unknown, for, when liberated from its salts, it at once breaks down into  $\text{SO}_2$ , S, and  $\text{H}_2\text{O}$ . The chief thiosulphate is the sodium salt ( $\text{Na}_2\text{S}_2\text{O}_3$ ), used extensively in photography because of its property of dissolving the halides of silver.

1. Dilute Hydrochloric Acid decomposes all thiosulphates with the evolution of sulphur dioxide and the separation of sulphur :—

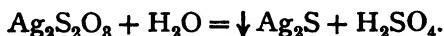


This reaction serves to distinguish this class of salts from sulphites, which do not give a separation of sulphur when so treated.

2. Silver Nitrate precipitates white silver thiosulphate, easily soluble in an excess of sodium thiosulphate with the formation of a complex salt :—



Boiling decomposes the double salt with the separation of silver sulphide and sulphur. Silver thiosulphate, almost as soon as formed, owing to its instability, becomes yellow, then brown, and finally black, with the formation of  $\text{Ag}_2\text{S}$  :—



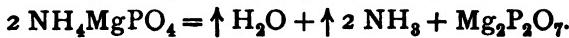
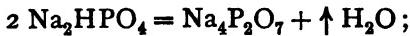
### PHOSPHATES

Three phosphoric acids are known, viz., orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ), metaphosphoric acid ( $\text{HPO}_3$ ), and pyrophosphoric acid ( $\text{H}_4\text{P}_2\text{O}_7$ ). The most stable in solution, as well as the most important of these, is the ortho-acid. The others are converted into this form by boiling with water, for example :—



Metaphosphoric acid, or the acetic acid solution of a metaphosphate, is distinguished from the other two by its characteristic property of coagulating albumen.

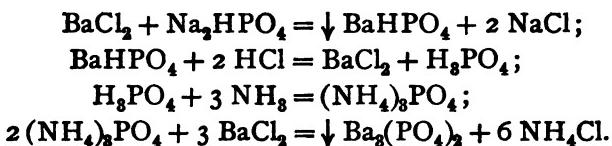
Pyrophosphoric acid and its salts are formed by heating the ortho- acid or its mono-hydrogen or mono-ammonium salts; thus :—



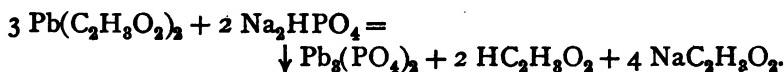
X

With the exception of the alkali salts, all normal pyro- and ortho-phosphates are insoluble in water. All of the phosphates of the metals of Group IV. are soluble in acetic, hydrochloric, and nitric acids. Those of the trivalent metals of Group III. are insoluble in acetic but soluble in hydrochloric acid.

1. **Barium Chloride** ( $\text{BaCl}_2$ ) precipitates from neutral solutions of orthophosphates white  $\text{BaHPO}_4$ , soluble in acetic, hydrochloric, and nitric acids ; from the acid solution, ammonia precipitates the tertiary phosphate :—



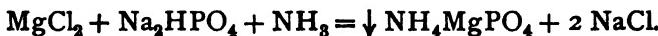
2. **Lead Acetate** [ $\text{Pb}(\text{C}_2\text{H}_8\text{O}_2)_2$ ] precipitates white lead phosphate, practically insoluble in acetic acid though soluble in nitric acid :—



3. **Silver Nitrate** precipitates only from strictly neutral solutions yellow silver phosphate ( $\text{Ag}_3\text{PO}_4$ ), soluble in mineral acids ;\* it is also soluble in acetic acid and in ammonium hydroxide.



4. **Magnesium mixture** ( $\text{MgCl}_2 + \text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$  in slight excess) precipitates from solutions of orthophosphates, white crystalline ammonium magnesium phosphate ( $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$ ) :—



The precipitate is soluble in acids, including acetic acid ; from solutions of the latter ammonium hydroxide reprecipitates the double phosphate (method of purification and separation from  $\text{AlPO}_4$ , which is insoluble in acetic acid). The precipitate is slightly soluble in water, but is insoluble in 2.5 per cent. ammonia water. From very dilute solutions, the precipitate

\* With HCl, a white precipitate of  $\text{AgCl}$  is obtained.

separates only on standing; on ignition, it yields magnesium pyrophosphate ( $Mg_2P_2O_7$ ). For further details concerning the precipitate, see reaction 4 under *Magnesium*. Arsenates yield a similar precipitate, but the latter is rendered reddish brown on treatment with silver nitrate, due to its conversion into silver arsenate ( $Ag_3AsO_4$ ).

5. **Ammonium Molybdate**, when added to a warm nitric acid solution of a phosphate, yields a canary-yellow precipitate of ammonium phosphomolybdate of variable composition  $[(NH_4)_8PO_4 \cdot 12 MoO_3]$ . Precipitation may be hastened by heating and by having an excess of ammonium nitrate present. The precipitate is soluble in excess of phosphoric acid or of alkali acid phosphate; hence, to secure complete precipitation, a large excess of the reagent is necessary. It is also soluble in alkalies, including ammonium hydroxide.

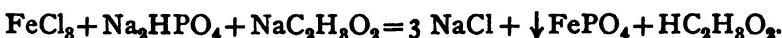
Arsenic acid yields a similar compound with this reagent, but the precipitate forms more slowly and requires a higher temperature for its complete precipitation.

This reaction affords a means of quantitatively separating phosphoric acid from the metals with which it may be combined.

6. **Ferric Chloride**, when added to a soluble phosphate not too strongly acid, yields a buff-colored precipitate of ferric phosphate ( $FePO_4$ ):—



As ferric phosphate is soluble in hydrochloric acid, the precipitation by ferric chloride in the above reaction is never complete; by adding an excess of sodium acetate, however, the hydrochloric acid is replaced by acetic acid, in which  $FePO_4$  is insoluble, and, as a consequence, precipitation is rendered complete:—



This reaction is utilized in removing phosphoric acid from solutions.

7. **Metallic Tin**, when added to a nitric acid solution of a phosphate, precipitates the phosphate as stannic phosphate, the

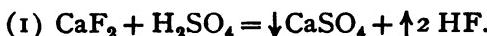
excess of the tin separating at the same time as insoluble metastannic acid. This reaction, like the one above, may be employed for the separation of the  $\text{PO}_4$  radical from the metals.

### FLUORIDES

Hydrogen fluoride, the water solution of which is hydrofluoric acid, at  $19.5^\circ \text{ C}$ . is a colorless, highly corrosive liquid. Its aqueous solutions attack the skin, producing painful sores; it must therefore be handled with care. As its chief property is its ability to etch glass, it must be kept in ceresine, hard rubber, or platinum vessels. With bases, it yields salts, known as *fluorides*.

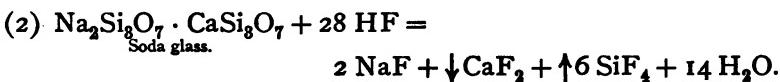
The fluorides of the alkali metals, with the exception of that of lithium, are soluble in water. Those of the alkaline earth group are either insoluble or sparingly soluble in water. The fluorides of Cu, Pb, Zn, and many other heavy metals, are only slightly soluble, while those of Al, Ni, Co, Ag, Sb, and Sn (-ous) dissolve readily.

1. Concentrated  $\text{H}_2\text{SO}_4$  decomposes most fluorides with the liberation of hydrogen fluoride:—

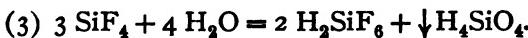


The reaction proceeds more rapidly if the mixture is heated. The HF may be recognized by its ability to etch glass (see reaction 2).

If the reaction is carried out in a test tube, the hydrofluoric acid which is set free attacks the glass, with the evolution of silicon tetrafluoride:—



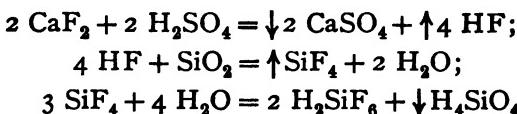
When brought in contact with water, silicon tetrafluoride reacts according to the following equation:—



The above three reactions may be utilized in testing for a fluoride. One need only heat the substance in a test tube with concentrated  $\text{H}_2\text{SO}_4$  and then hold in the escaping vapors a

drop of water held on the loop of a platinum wire. In the presence of a fluoride, the "water bead" will become turbid owing to the formation of gelatinous silicic acid. The test may also be carried out in lead or platinum vessels, if the fluoride is first intimately mixed with ignited silica ( $\text{SiO}_2$ ) before the treatment with concentrated  $\text{H}_2\text{SO}_4$ .

The reactions are as follows:—



**2. The Etching Test.** This test, as explained above, is based on the property possessed by hydrofluoric acid to dissolve  $\text{SiO}_2$  or glass. In a platinum crucible or lead dish, mix, with the aid of a piece of wood, some of the powdered substance with concentrated sulphuric acid. Cover with a watch glass that has been coated on the convex side with paraffine and through which some characters have been scratched. Put a little water on the upper concave side of the watch glass to prevent the paraffine from melting during the heating, and gently heat the crucible or dish, preferably on a water bath. After some time, remove the watch glass, warm it, and wipe the paraffine off. If a fluoride is present in the substance under examination, the glass will be corroded or etched in those places where the glass has been exposed to the liberated hydrofluoric acid. It is evident that this test is inapplicable in the presence of silicates. Anhydrous HF does not etch glass.

**3. Calcium Chloride**, added to an aqueous solution of a fluoride, gives a white gelatinous precipitate of calcium fluoride ( $\text{CaF}_2$ ), soluble with difficulty in  $\text{HCl}$  and  $\text{HNO}_3$ , but practically insoluble in acetic acid. From the acid solution of calcium fluoride, ammonium hydroxide does not reprecipitate the fluoride, because of the solubility of  $\text{CaF}_2$  in ammonium salts.

**4. Fusion with Sodium Carbonate** only partially decomposes  $\text{CaF}_2$ . In the presence of silica, however, the decomposition may be rendered complete.

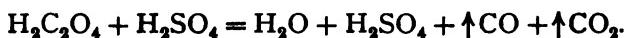
### OXALATES

With the exception of those of the alkali metals, magnesium and chromium, nearly all the oxalates are insoluble or sparingly soluble in water; they all are soluble in mineral acids and in many cases in an excess of alkali oxalate with the formation of double salts.

1. **Barium Chloride** precipitates white barium oxalate ( $\text{BaC}_2\text{O}_4$ ), soluble in oxalic and acetic acids.

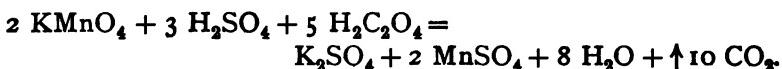
2. **Calcium Sulphate** or **Calcium Chloride** precipitates white crystalline  $\text{CaC}_2\text{O}_4$ , insoluble in oxalic and acetic acids, and in ammonium oxalate, but soluble in hydrochloric acid. As  $\text{CaC}_2\text{O}_4$  is one of the most insoluble of the oxalates,  $\text{CaSO}_4$  is an excellent reagent for the detection of this acid.

3. **Concentrated Sulphuric Acid**, when added to an oxalate in the solid state, decomposes it with the evolution of CO and  $\text{CO}_2$  :—



If the mixed gases are passed through limewater or sodium hydroxide, the  $\text{CO}_2$  will be absorbed and the escaping CO may be recognized by the characteristic blue flame with which it burns.

4. **Potassium Permanganate Solution**, when added to a hot sulphuric acid solution of an oxalate, is bleached because of its reduction to a manganous salt, the oxalic acid being oxidized at the same time to  $\text{CO}_2$  and water :—



5. **Behavior of Oxalates on Ignition.** At a red heat, all oxalates are, decomposed with the evolution of CO and  $\text{CO}_2$ . The oxalates of the alkalies and alkaline earths are converted by ignition into carbonates with little or no carbonization. Magnesium oxalate yields  $\text{MgO}$  when heated. All other oxalates leave either a residue of metal or an oxide, depending upon the ease with which the oxide is reduced.

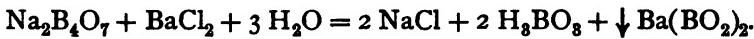
An oxalate may be decomposed by evaporating it with a mixture of  $H_2SO_4$  and  $HNO_3$  until  $SO_3$  fumes are given off; any organic matter present will also be destroyed at the same time.

### BORATES

Boron forms three acids, namely, orthoboric acid ( $H_3BO_3$ ), metaboric acid ( $HBO_2$ ), and tetraboric acid ( $H_2B_4O_7$ ); the last two may be obtained from the first by careful heating. Salts of the ortho-acid hydrolyze in a water solution, so that the salts of boric acid we are concerned with are either of the meta- or pyro-type. Borates of the alkali metals alone are soluble in water, yielding solutions which have an alkaline reaction owing to partial hydrolysis; all other borates are either insoluble or sparingly soluble in water, but are readily soluble in mineral acids and in ammonium salts.

**1. Turmeric Paper Test.** If a piece of turmeric paper is dipped into a solution of a borate slightly acid with  $HCl$ , and the paper is then dried by placing it on a watch glass and heating the latter on a water or steam bath, the paper assumes a reddish brown color. If the paper is now moistened with a drop of caustic soda solution, the color changes to a greenish black.

**2. Barium Chloride** precipitates from concentrated solutions flocculent barium metaborate, soluble in excess of barium chloride, in ammonium chloride, and in acids:—



**3. Calcium Chloride** gives with borates reactions precisely similar to those produced by  $BaCl_2$ .

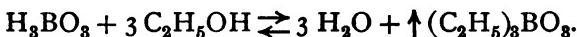
**4. Silver Nitrate** precipitates from cold concentrated solutions white silver metaborate ( $AgBO_2$ ), soluble in ammonium hydroxide and nitric acid; warming converts it into brown silver oxide ( $Ag_2O$ ).

**5. Flame Tests.** Free boric acid and some of its volatile compounds, e.g., the fluoride ( $BF_3$ ), its esters, as  $(CH_3)_2BO_3$  and

$(C_2H_5)_3BO_3$ , when brought into the bunsen flame, impart to it a characteristic green color.

6. **Concentrated Sulphuric Acid**, when added to a borate, decomposes it with the liberation of free boric acid ( $H_3BO_3$ ). The test depending upon this and the above reactions is carried out by making a paste of the substance with concentrated  $H_2SO_4$ , taking up some of the mixture on the loop of a platinum wire, and holding it in the flame, when, if a borate is present in the substance being examined, the characteristic green color will be observed. This test does satisfactorily for most borates. For silicates containing boron, which are not decomposed by concentrated  $H_2SO_4$ , it is necessary to mix the mineral with a little calcium fluoride before adding the sulphuric acid; under these conditions, volatile boron fluoride ( $BF_3$ ) is formed, which, when brought into the bunsen flame, colors it green.

7. **Concentrated  $H_2SO_4$  and Alcohol.** If concentrated sulphuric acid is added to a borate and then a little methyl or ethyl alcohol, and the mixture is stirred and lighted, the resulting flame will be found to be green at its borders, due to the formation of volatile methyl or ethyl borate:—



The concentrated  $H_2SO_4$  performs the double function of liberating the boric acid and absorbing the water formed in the above reversible reaction, thus causing the latter to proceed from left to right.

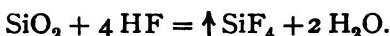
8. **Behavior on Ignition.** Borates of the alkali metals, when heated, swell up (escaping of water), and finally fuse with the formation of a colorless glass; the latter, possessing as it does an excess of acid oxide, readily unites with metallic oxides on heating, with the formation of metaborates (borax beads) having characteristic colors. Thus, with cobalt oxide or any cobalt compound we obtain



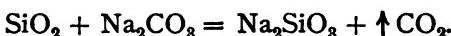
The cobalt metaborate is blue.

## SILICATES

Silica ( $\text{SiO}_2$ ), the anhydride of silicic acid, occurs abundantly in a more or less pure state in nature as quartz, rock crystal, flint, agate, sand, etc. It is insoluble in water and in all acids with the exception of hydrofluoric acid; the latter dissolves it with the formation of gaseous silicon tetrafluoride ( $\text{SiF}_4$ ):—

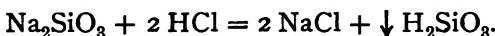


To expel silica completely with HF, the presence of concentrated  $\text{H}_2\text{SO}_4$  is necessary. When silica is fused with sodium carbonate and the mass is extracted with water, a solution of sodium silicate is obtained :—



All silicates are insoluble in water with the exception of those of sodium and potassium, which are soluble in water in the presence of free alkali.

i. If to a solution of sodium or potassium silicate, hydrochloric or nitric acid is added until an acid reaction results, part of the silicic acid will separate out as a gelatinous precipitate, while the rest will remain in solution in the form of a hydrosol :—



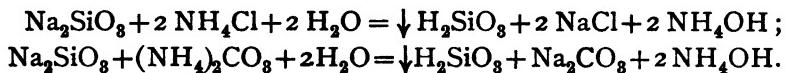
If the sodium silicate solution is very dilute, the silicic acid set free may remain entirely in solution.

Precipitated silicic acid is somewhat soluble in water and in acids, and is readily soluble in alkali hydroxides and carbonates.

If an acid solution of an alkali silicate, which may contain more or less of precipitated silicic acid in suspension, is evaporated to dryness on a boiling water bath, the precipitated, as well as the dissolved, silicic acid loses water and becomes insoluble in acids; therefore, on extracting the dried residue with hydrochloric acid and filtering, practically all the silicic acid (about 99 per cent.) will be left on the filter in a more or less dehydrated state. The more complete the dehydration, the more insoluble does the resulting silicic acid become. This property of silicic acid of becoming insoluble in acids on dehydration is

of great analytical importance, since it enables the analyst, early in the analysis, to completely separate the silicic acid from the metals with which it was originally combined.

2. **Ammonium chloride or ammonium carbonate**, when added to a solution of alkali silicate, causes a precipitation of metasilicic acid :—

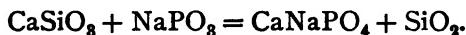


3. **Barium Chloride** precipitates white  $\text{BaSiO}_3$ , soluble in acids.

4. **Silver Nitrate** precipitates yellow  $\text{Ag}_2\text{SiO}_3$ , soluble in acids and in ammonium hydroxide.

5. **Ammonium Molybdate** solution containing an excess of nitric acid yields, with solutions of silicates, a yellow solution. On heating in the presence of much  $\text{NH}_4\text{Cl}$ , a canary-yellow precipitate is produced.

6. **Sodium Metaphosphate Bead Test.** When a silicate is fused in a metaphosphate bead prepared from microcosmic salt ( $\text{NH}_4\text{NaHPO}_4$ ), the bases are dissolved to a transparent bead, while the silica in the form of a "skeleton" of the original mass remains undissolved as an opaque body :—



#### *Treatment of Insoluble Silicates*

(a) **Silicates decomposed by Acids** (not including hydrofluoric acid). The finely ground silicate \* is heated in a casserole with

\* **Powdering Minerals.** Since substances are more readily soluble in a state of fine powder than in the form of lumps, the process of powdering is always resorted to before the analysis of minerals, slags, and ores is begun. This is accomplished by first wrapping up in a clean towel a number of selected specimens of the substance, placing the latter on a plate of hard steel and breaking them up with several sharp blows from a hard steel hammer. The resulting mixture of powder and coarse particles is then introduced into a diamond steel mortar, in small portions at a time, and crushed to a coarse powder; the latter is then thoroughly mixed, and about two grams or more are reduced to an extremely fine state of division by grinding in an agate mortar until the entire quantity passes through a 100-mesh sieve.

concentrated HCl \* and is boiled until decomposition is complete. As a result of the action of the acid, part of the silicic acid separates in the gelatinous form. The mixture is then evaporated to dryness, preferably on a steam bath, and the silica is completely dehydrated by heating the nearly dry mass in an air oven maintained at 120° C. until no more acid fumes are given off. The dried residue is first treated with 10 cc. of concentrated HCl and heated to dissolve the bases, some of which may have been rendered difficultly soluble by the dehydration process; water is then added, the mixture is heated again with stirring, and finally is filtered. The filtrate will contain all of the metals in the form of chlorides. The residue will contain practically all of the silicic acid and may be contaminated with small amounts of the bases, chiefly iron and aluminum as oxides. To test the purity of the silicic acid, the precipitate and a portion of the filter retaining the precipitate are placed in a platinum crucible, moistened with a little concentrated ammonium nitrate solution to facilitate the combustion of the filter, and ignited until all of the paper is consumed. The crucible is then carried to the hood, placed on a pipestem triangle, and is treated with a few drops of concentrated H<sub>2</sub>SO<sub>4</sub> and about 5 cc. of hydrofluoric acid. It is then gently heated to dryness and finally ignited. By this treatment all the silicic acid will be driven off as SiF<sub>4</sub>. Any residue is treated according to page 197 for insoluble substances.†

(b) Silicates which are slightly or not attacked appreciably by acids in the above treatment are decomposed by fusing them in a platinum crucible, *unless reducible metals are shown to be present*, with ten times their weight of a mixture of sodium and potassium carbonates until the mass is in a state of quiet fusion. By this treatment, the silica will be converted into sodium silicate, while the bases will be variously converted into carbonate, oxide, or metal, depending upon their nature. After cooling, the crucible with its contents is placed in a casserole or

\* When metals of the first group are known to be present, it is preferable to use nitric acid.

† The residue may consist of Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, or BaSO<sub>4</sub>, or of all three substances.

evaporating dish, and is treated with an excess of hydrochloric acid.\* The latter takes the bases into solution and at the same time decomposes the alkali silicate with a partial precipitation of silicic acid. The mixture is then evaporated to dryness, dehydrated at 120° C., extracted with hot concentrated acid, diluted with water, and the silicic acid is filtered off and purified as already outlined. The filtrate is examined for bases and acids except those removed by the above treatment (see page 167).

(c) **Decomposition of Silicates with Hydrofluoric Acid.** *Under a hood*, treat about one gram of the finely powdered mineral contained in a platinum crucible or dish with about 10 cc. of hydrofluoric acid and 2 cc. of concentrated  $H_2SO_4$ , and evaporate on a hot plate until  $SO_3$  fumes are evolved. By this procedure, the silicate will be decomposed and the metals are left as sulphates.

**Treatment for the Detection of Alkalies in Silicates.** If undecomposed by acids, except hydrofluoric, apply J. Lawrence Smith's method, which is given under the head of "Insoluble Substances." The hydrofluoric acid method is also suitable for the detection of the alkalies in insoluble silicates.

### TARTRATES

**Solubilities.** The normal tartrates of the alkali metals, as well as those of aluminum and ferric iron, are soluble in water; nearly all others are insoluble in water, but are soluble in hydrochloric and nitric acids, and for the most part are soluble in an excess of alkali tartrate with the formation of double salts.

1. **Concentrated Sulphuric Acid**, when added to a tartrate and the mixture is heated, causes a charring with the evolution of  $SO_2$ .

2. **Silver Nitrate** does not react with free tartaric acid, but from solutions of normal tartrates it precipitates white curdy silver tartrate ( $Ag_2C_4H_4O_6$ ), readily soluble in nitric acid and ammonium hydroxide. If the tube containing the ammoniacal solution of silver tartrate is heated gently, preferably in a boil-

\* If metals of Group I. are known to be present, it is preferable to use nitric acid.

ing water bath, a deposit of silver forms on the sides of the tube in the form of a mirror.

3. **Calcium Chloride**, added in excess to a concentrated solution of a neutral tartrate, precipitates white crystalline calcium tartrate ( $\text{CaC}_4\text{H}_4\text{O}_6$ ), soluble in acids, including acetic acid; the precipitate is soluble in cold caustic soda free from carbonate, from which, on boiling,  $\text{CaC}_4\text{H}_4\text{O}_6$  reprecipitates in a gelatinous form which redissolves on cooling. The precipitation of calcium tartrate is interfered with by the presence of ammonium salts. If  $\text{CaCl}_2$  is not added in excess, a white amorphous precipitate forms; this dissolves in excess of the normal tartrate with the formation of a double salt.

4. **Potassium Salts**, when added to a neutral solution of a tartrate, give no precipitate; if, however, the resulting solution is rendered acid with acetic or citric acid, a crystalline precipitate of "cream of tartar" forms at once or after some time, depending upon the concentration of the tartrate solution. For properties of this salt, see reaction 2 under *Potassium*. Free tartaric acid or sodium acid tartrate solutions of moderate strengths give an immediate precipitate with potassium salts.

5. **Behavior on Ignition.** Tartaric acid and tartrates, when heated, decompose with the evolution of inflammable vapors possessing the odor of burnt sugar; a carbonaceous residue is left at the same time, consisting of carbon in the case of tartaric acid or of a mixture of carbon and alkali carbonate in the case of alkali tartrates. The heavy metal tartrates on heating may leave a residue consisting of the oxide of the metal or of the metal itself.

#### CHROMATES

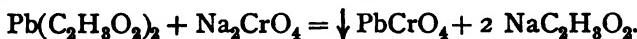
Chromic acid and chromates have already been mentioned in connection with the metal chromium (see page 74). They are all red or yellow.

**Solubilities.** The chromates of the alkalies, magnesium and calcium, are soluble in water. Nearly all the others are insoluble; most of these dissolve in nitric acid. The acid solutions are

always red, owing to the presence of a dichromate. The color of chromates, even in very dilute solutions, is easily visible, and hence, in the absence of other colored substances, furnishes a delicate test for their presence. For a discussion of the reduction of chromates to chromic salts and of the oxidation of the latter to chromates, see under *Chromium*, pages 76 and 74.

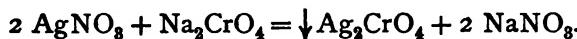
**1. Barium Chloride** precipitates yellowish white barium chromate ( $\text{BaCrO}_4$ ), difficultly soluble in water but soluble in hydrochloric and nitric acids. For other properties, see reaction 5 under *Barium*.

**2. Lead Acetate** precipitates from neutral or acetic acid solutions yellow lead chromate ( $\text{PbCrO}_4$ ) :—

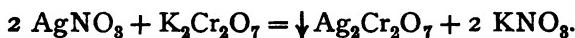


This is practically insoluble in water, acetic acid, and ammonium hydroxide, but is soluble in caustic soda solution, from which acetic acid reprecipitates the chromate; it is also soluble in nitric acid.

**3. Silver Nitrate** precipitates from strictly neutral solutions purplish red silver chromate :—



Silver chromate is readily soluble in nitric acid and ammonium hydroxide. From slightly acid concentrated solutions a reddish brown crystalline precipitate of  $\text{Ag}_2\text{Cr}_2\text{O}_7$  is formed which possesses about the same solubilities as  $\text{Ag}_2\text{CrO}_4$  :—

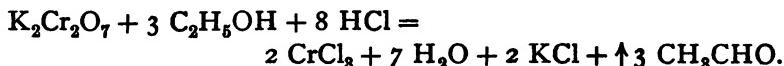


The chromates of silver are readily converted into the chloride by treatment with HCl.

**4. Potassium Iodide**, when added to a dichromate or a nitric acid solution of a chromate, is oxidized with the liberation of iodine; a drop of  $\text{CS}_2$ , when added and shaken with the mixture, acquires a violet color, due to the extraction of iodine. The chromic acid is reduced at the same time.

**5. Ethyl Alcohol** ( $\text{C}_2\text{H}_5\text{OH}$ ), when added to a chromate solution acidified with HCl or  $\text{H}_2\text{SO}_4$ , and the mixture is boiled,

causes a reduction of the chromate to a chromic salt, as indicated by a change in color of the solution from orange-red to green. The alcohol is oxidized at the same time to acetaldehyde:—



This method is frequently used to reduce chromates to chromic salts before treating a solution containing a chromate with  $\text{H}_2\text{S}$ . For the equation for the reduction of chromates by concentrated HCl, see page 76.

**6. Hydrogen Dioxide Test.** If to a mixture consisting of 5 cc. of dilute hydrogen dioxide solution, slightly acid with dilute sulphuric acid, and 2 cc. of ether, a little chromate solution is added, and the mixture is shaken, the ether layer will acquire an intense blue color, due to the presence of some such additive compound as  $\text{CrO}_3 \cdot \text{H}_2\text{O}_2$ , which, however, is very unstable. One part of  $\text{K}_2\text{CrO}_4$  in 40,000 parts of water is said to be the sensitiveness of this reaction.

**7. Insoluble Chromium Compounds,** when fused with sodium carbonate to which a little potassium chlorate has been added, and the mass is extracted with water, will yield an aqueous solution containing the chromium as chromate, while the residue will contain the other metals. (Note, however, the conduct of Manganese under similar conditions.)

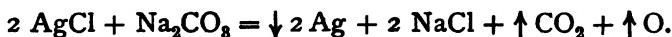
## GROUP II

This group comprises those acids which yield with silver nitrate precipitates insoluble in nitric acid.  $\text{BaCl}_2$  does not precipitate them.

### CHLORIDES

**Solubilities.** All chlorides are soluble in water with the exception of those of silver, copper(-ous), and mercury(-ous). The oxychlorides of mercury(-ic), bismuth, and antimony are also insoluble. Lead chloride is sparingly soluble in cold water. The normal chlorides of bismuth and antimony require the presence of free acid to keep them in solution. All insoluble

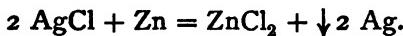
chlorides dissolve in *aqua regia* with the exception of silver chloride. Fusion with sodium carbonate transposes \* all insoluble chlorides :—



The chlorides of barium, sodium, and potassium are practically insoluble in concentrated hydrochloric acid.

1. **Silver Nitrate** precipitates from nitric acid solutions, white, curdy silver chloride ( $\text{AgCl}$ ), which darkens on exposure to light; the precipitate is soluble in ammonium hydroxide and carbonate, sodium thiosulphate, and potassium cyanide.

Besides the fusion method with sodium carbonate above mentioned, silver chloride may be tested for chlorine by treating it with zinc and sulphuric acid, and allowing the action to continue for several minutes. If, now, the mixture is filtered, the filtrate will contain the chlorine in the form of  $\text{ZnCl}_2$  :—

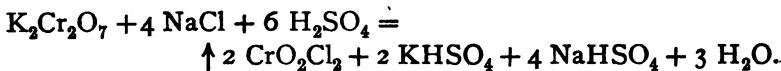


2. **Lead Acetate** precipitates white lead chloride ( $\text{PbCl}_2$ ). For its properties, see reaction 1 under *Lead*.

3. Concentrated  $\text{H}_2\text{SO}_4$  and  $\text{MnO}_2$ , when added to a chloride, and the mixture is heated, oxidize the chloride, with the evolution of chlorine; the latter is recognized by its color and odor as well as by its ability to bleach moist litmus or indigo paper :—

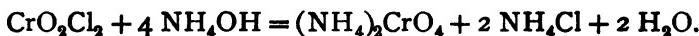


4. **Potassium Dichromate and Concentrated Sulphuric Acid.** If a dry mixture of a chloride and powdered  $\text{K}_2\text{Cr}_2\text{O}_7$  is treated with concentrated  $\text{H}_2\text{SO}_4$  and heated gently, chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ), a reddish brown gas, will be evolved :—



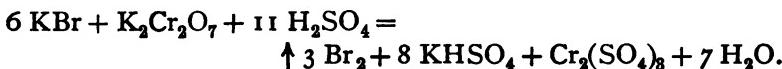
\* When an insoluble salt is treated with sodium carbonate, whereby the acid radical is converted into a soluble sodium salt, the compound is said to be *transposed*.

If the gas is absorbed by ammonium hydroxide, the latter will be colored yellow owing to the formation of ammonium chromate:—



The presence of chromic acid in the ammonium hydroxide solution may be shown by rendering it acid with acetic acid and adding  $\text{Pb}(\text{C}_2\text{H}_8\text{O}_2)_2$ , when a yellow precipitate of  $\text{PbCrO}_4$  will be obtained.

This test for a chloride is of special value, for by its means chlorides may be detected in the presence of bromides. Iodides, if present in not too large amounts, do not interfere. The reaction with the bromide is as follows:—



The liberated bromine does not color the ammonium hydroxide, and hence does not interfere with the test. Iodides behave in the same way as bromides.

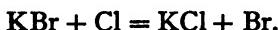
### BROMIDES

**Solubilities.** All bromides are soluble in water with the exception of those of silver, mercury (-ous), copper (-ous), and lead, the last being only sparingly soluble in cold water. Soluble bromides of the heavy metals are easily transposed by boiling with sodium carbonate solution. The insoluble bromides are tested for the halogen by fusion with  $\text{NaCO}_3$ , extracting the melt with water, and filtering. The filtrate will then contain the bromide as  $\text{NaBr}$ .

1. **Silver Nitrate** precipitates yellowish white silver bromide ( $\text{AgBr}$ ), which darkens on exposure to light; it is insoluble in nitric acid and in cold ammonium carbonate; it dissolves with difficulty in cold ammonium hydroxide, but easily in  $\text{KCN}$  and  $\text{Na}_2\text{S}_2\text{O}_8$ . Silver bromide may be decomposed by  $\text{Zn}$  and sulphuric acid in the same way as indicated for  $\text{AgCl}$ .

2. **Chlorine Water**, when added in small amounts to a solution of a bromide, decomposes it with the liberation of bromine. If

a few drops of carbon disulphide ( $\text{CS}_2$ ) or chloroform ( $\text{CHCl}_3$ ), in which bromine is soluble, are added, and the mixture is shaken, the  $\text{CS}_2$  or  $\text{CHCl}_3$  will acquire a yellow or reddish color, depending upon the amount of bromine present. The test is exceedingly sensitive; 1 part of bromine in 1000 parts of water suffices to give a distinctly visible result.



Care must be exercised in performing the test to add the chlorine water one drop at a time, and to shake after each addition; for, if an excess is added, colorless bromine chloride ( $\text{BrCl}$ ) may form.

3. **Potassium Dichromate**, in the presence of cold dilute sulphuric acid, does not liberate bromine from bromides (distinction from iodides).

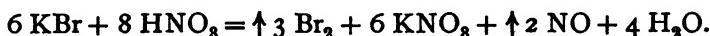
4. **Concentrated  $\text{H}_2\text{SO}_4$** , when added to a bromide, and the mixture is heated, causes the liberation of bromine with hydrobromic acid.

5. **Concentrated  $\text{H}_2\text{SO}_4$  and  $\text{MnO}_2$** , when added to a bromide, and the mixture is heated, causes the liberation of bromine; the latter is recognized by its color, odor, and by its property of turning starch yellow and starch-iodide paper blue.

6. **Potassium Nitrite**, when added to a bromide acidified with dilute sulphuric acid, does not liberate bromine (distinction from iodides).

7. **Potassium Permanganate**, when added to a bromide solution acid with sulphuric acid, and the mixture is boiled, causes the liberation of bromine, recognizable by its odor, color, and by its ability to turn starch-iodide paper blue.

8. **Nitric Acid** decomposes bromides, with the exception of  $\text{AgBr}$ , on heating, with the liberation of bromine:—



#### IODIDES

**Solubilities.** With the exception of  $\text{HgI}_2$ ,  $\text{HgI}$ ,  $\text{AgI}$ ,  $\text{CuI}$ , and the sparingly soluble  $\text{PbI}_2$ , all iodides are soluble in water.

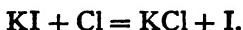
Some of the insoluble ones dissolve in an excess of alkali iodide with the formation of double salts. Soluble iodides of the heavy metals are best tested for the halogen by first transposing by boiling with sodium carbonate solution. The insoluble iodides — like the insoluble chlorides and bromides — are best transposed by fusion with sodium carbonate.

1. **Silver Nitrate**, when added to a solution of an iodide, precipitates yellow amorphous silver iodide ( $\text{AgI}$ ), insoluble in nitric acid, and only very sparingly soluble in ammonium hydroxide and cold ammonium carbonate (distinction from chlorides). It is soluble in potassium cyanide and sodium thiosulphate solutions. Silver iodide may be decomposed by  $\text{Zn}$  and  $\text{H}_2\text{SO}_4$  in the manner indicated for  $\text{AgCl}$  and  $\text{AgBr}$ .

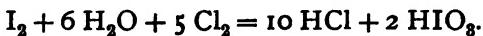
2. **Concentrated  $\text{H}_2\text{SO}_4$** , acting alone on an iodide, yields hydriodic acid and iodine, mixed with various reduction products of sulphuric acid, depending upon the temperature and the relative proportions of acid and iodide.

3. **Concentrated  $\text{H}_2\text{SO}_4$  and Manganese Dioxide**, when added to an iodide, and the mixture is heated, liberate iodine. The reaction is similar to those in which  $\text{Br}$  and  $\text{Cl}$  are set free by the same reagents.

4. **Chlorine Water**, when added drop by drop to a solution of an iodide, decomposes it with the liberation of iodine :—



The free iodine may be recognized by shaking the mixture with a few drops of  $\text{CS}_2$  or  $\text{CHCl}_3$ ; the latter solvents will extract the iodine and acquire a reddish violet color. Free iodine may also be identified by the blue colored compound it yields when treated with starch paste. In liberating iodine with chlorine water, care must be taken to avoid adding an excess, otherwise the liberated iodine will be oxidized to colorless iodic acid :—



5. **Potassium Nitrite**, when added to a solution of an iodide acid with sulphuric acid, causes the separation of iodine, recognized by coloring  $\text{CS}_2$  violet or starch paste blue.

In carrying out the starch-iodide reaction, it is important to have the iodine solution very dilute; if it is at all concentrated, a nearly black precipitate, instead of a fine blue coloration, will be obtained. Potassium nitrite has an advantage over chlorine as an iodine liberator, as an excess does not hinder the reaction.

6. **Cupric Salts**, when added to a solution of an iodide, yield a dirty brown precipitate of cuprous iodide ( $\text{CuI}$ ); at the same time iodine is set free : —



7. **Ferric Salts** also liberate iodine from iodides, being at the same time reduced to the ferrous state : —

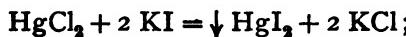


8. **Potassium Dichromate**, when added to an iodide solution acid with sulphuric acid, causes iodine to be set free : —



In all of the above cases the liberated iodine may be detected by shaking the mixture with one cc. of  $\text{CHCl}_3$  or  $\text{CS}_2$ , which acquires a violet color.

9. **Mercuric Chloride**, when added to an iodide solution, precipitates scarlet mercuric iodide ( $\text{HgI}_3$ ), soluble in an excess of alkali iodide : —



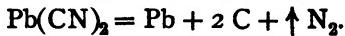
### CYANIDES

**Solubilities.** The alkali and alkaline earth cyanides and mercuric cyanide are soluble in water; nearly all others are insoluble. The cyanides of the heavy metals dissolve in an excess of alkali cyanide with the formation of complex double salts.

Heated with exclusion of air, the cyanides of the alkalies and alkaline earths fuse without decomposition. In contact with air, they oxidize with the formation of cyanate : —



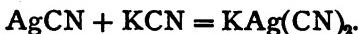
It is in consequence of the readiness with which they oxidize that the reducing power of cyanides is due. The cyanides of the heavy metals when heated in a closed tube undergo decomposition, the products varying with the nature of the metal:—



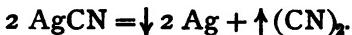
**CAUTION:** All tests for cyanides which involve the evolution of a gas should be performed under the hood.

The cyanides of the noble metals on heating break up into the metal and cyanogen gas. By this means, the cyanides of silver and mercury allow themselves to be readily detected. Mercuric cyanide differs in many respects from the other water-soluble simple cyanides. It does not yield a precipitate with silver nitrate and is not decomposed by cold dilute sulphuric acid; it is, however, decomposed by  $\text{H}_2\text{S}$  with the precipitation of mercuric sulphide and the production of HCN.

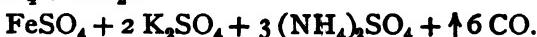
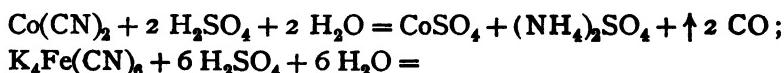
1. **Silver Nitrate**, when added to a simple cyanide, excepting  $\text{Hg}(\text{CN})_2$ , yields a white precipitate of silver cyanide ( $\text{AgCN}$ ), easily soluble in excess of alkali cyanide with the formation of a double cyanide:—



$\text{AgCN}$  is also soluble in ammonium hydroxide and in sodium thiosulphate, but is insoluble in nitric acid. On ignition, it is decomposed with the evolution of cyanogen gas and the separation of silver:—



2. **Sulphuric Acid**, dilute, when added to a solution of a cyanide [except  $\text{Hg}(\text{CN})_2$ ], decomposes it with the liberation of HCN, readily recognized by its odor. If the dilute acid is heated, it is capable of decomposing the insoluble cyanides. If the acid is concentrated and hot, it will attack all cyanides whether simple or complex:—



The above equations, which are typical, show that the metals are converted into sulphates, that carbon monoxide is produced, and that all the nitrogen is converted into ammonium sulphate.

**3. Formation of Ferrocyanide.** If a solution containing an alkali cyanide is made strongly alkaline with sodium hydroxide and a little ferrous sulphate and ferric chloride are added, and the mixture is gently heated and finally made acid with hydrochloric acid, a precipitate of prussian blue will be formed. The reactions which take place are the following:—

- (1)  $\text{FeSO}_4 + 2 \text{NaOH} = \downarrow \text{Fe(OH)}_2 + \text{Na}_2\text{SO}_4;$
- (2)  $\text{Fe(OH)}_2 + 2 \text{KCN} = \downarrow \text{Fe(CN)}_2 + 2 \text{KOH};$
- (3)  $\text{Fe(CN)}_2 + 4 \text{KCN} = \text{K}_4\text{Fe(CN)}_6;$
- (4)  $3 \text{K}_4\text{Fe(CN)}_6 + 4 \text{FeCl}_3 = \downarrow \text{Fe}_4[\text{Fe(CN)}_6]_3 + 12 \text{KCl}.$

**4. Formation of Thiocyanate.** To a solution of an alkali cyanide add a little  $(\text{NH}_4)_2\text{S}_2$ , and evaporate the solution on a water bath to dryness. The residue, which will now consist of ammonium thiocyanate ( $\text{NH}_4\text{SCN}$ ), is treated with one or two drops of dilute HCl, partly to insure the destruction of any undecomposed sulphide and partly because the presence of hydrochloric acid assists the final reaction [see reaction 5 under *Iron (-ic)*]; if a drop of ferric chloride is now added, a blood-red coloration will be produced because of the formation of ferric thiocyanate  $[\text{Fe}(\text{SCN})_6]$ .

If it is desired to detect hydrocyanic acid evolved from an insoluble cyanide on treatment with hot dilute  $\text{H}_2\text{SO}_4$ , cover the test tube containing the mixture with a crucible cover, on the under side of which has been placed a drop of  $(\text{NH}_4)_2\text{S}_2$ , and allow the action to continue for several minutes; then invert the cover and dry on the water bath, and proceed as directed above for the formation of ferric thiocyanate.

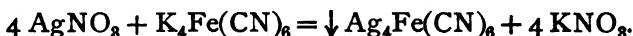
#### FERROCYANIDES

Hydroferrocyanic acid  $[\text{H}_4\text{Fe}(\text{CN})_6]$  is a colorless crystalline solid, easily soluble in water; on exposure to air the solution

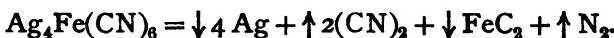
becomes blue from decomposition. The salts of ferrocyanic acid are much more stable than the acid.

**Solubilities.** The ferrocyanides of the alkalies and alkaline earth metals are soluble in water; nearly all the others are insoluble or sparingly soluble in water and in cold dilute acids.

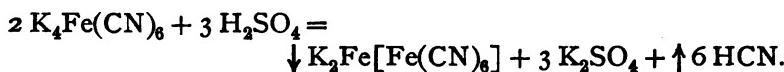
1. **Silver Nitrate** precipitates white silver ferrocyanide, insoluble in dilute nitric acid and in ammonium hydroxide, but soluble in potassium cyanide solution:—



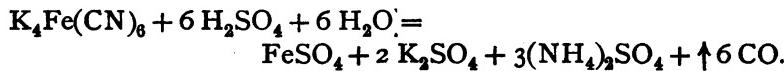
On ignition, the precipitate is decomposed with the separation of silver and evolution of cyanogen gas:—



2. **Sulphuric Acid**, when cold and dilute, does not decompose ferrocyanides; on heating to boiling, however, partial decomposition sets in with the liberation of part of the cyanogen as hydrocyanic acid:—

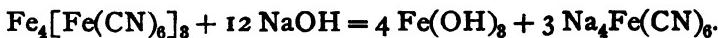


Concentrated sulphuric acid, when heated, completely decomposes ferrocyanides with the evolution of carbon monoxide:—



3. **Ferric Salts**, added to a slightly acid solution of a ferrocyanide, yield a precipitate of prussian blue.

4. The Solution of Insoluble Ferrocyanides is accomplished by boiling the compound with sodium hydroxide and filtering, when the metal will be left on the filter in the form of hydroxide, while the filtrate will contain the acid radical in the form of sodium ferrocyanide:—



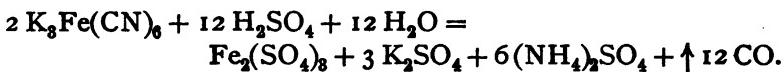
The residue is dissolved in acid and the metal is tested for in the solution obtained. The filtrate is acidified with HCl and tested for the ferrocyanogen radical by adding ferric chloride.

If the metal is one whose hydroxide is soluble in excess of sodium hydroxide, as Zn, it may be separated from the ferrocyanide by passing carbon dioxide into the alkaline solution, boiling, and then filtering off the basic carbonate of zinc. In the case of lead ferrocyanide, the lead may be precipitated from the alkaline solution by a stream of  $H_2S$ .

Fusion with sodium carbonate decomposes ferrocyanides.

### FERRICYANIDES

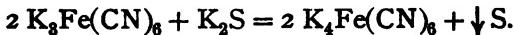
**Solubilities.** All ferricyanides are insoluble in water and in cold dilute acids with the exception of those of the alkalies and alkaline earths. Heated to redness, ferricyanides decompose, the products being iron carbide, cyanide, nitrogen, and cyano-gen; the last burns with a characteristic purplish flame. Sulphuric acid, when dilute and warm, causes partial decomposition with the evolution of HCN. When concentrated and hot, it effects a complete decomposition with the liberation of CO. The equation as given by Treadwell is as follows:—



1. **Silver Nitrate** gives with ferricyanides a reddish brown precipitate of silver ferricyanide, insoluble in nitric acid, but soluble in ammonium hydroxide and in potassium cyanide.

2. **Iron Salts.** Ferric salts give no precipitate, but a dark coloration; ferrous salts give a blue precipitate of Turnbull's blue,  $Fe_3[Fe(CN)_6]_2$ , insoluble in acids.

3. **Reducing Agents**, such as  $H_2S$ ,  $SO_2$ , and  $HI$ , readily reduce ferricyanides to ferrocyanides in alkaline solutions:—

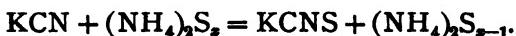


### THIOCYANATES

Alkali thiocyanates are readily prepared by heating the cyanide with sulphur:—



or by heating an alkali cyanide or hydrocyanic acid with ammonium polysulphide :—



**Solubilities.** Nearly all the thiocyanates are soluble in water with the exception of those of silver, mercury, copper, and gold.

1. **Silver Nitrate** precipitates white, curdy silver thiocyanate, insoluble in dilute nitric acid, but soluble with difficulty in ammonium hydroxide.

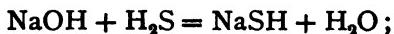
2. **Ferric Salts** give with alkali thiocyanate solutions a blood-red coloration, due to the formation of ferric thiocyanate. The color is destroyed by mercuric chloride.

### SULPHIDES

Hydrogen sulphide is a colorless gas having a characteristic and unmistakable odor. Its solution in water possesses a feeble acid reaction, but it is very unstable, oxidizing readily in contact with air with the separation of sulphur :—



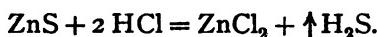
$\text{H}_2\text{S}$  reacts with bases forming hydrosulphides and sulphides, which, if  $\text{H}_2\text{S}$  is looked upon as a dibasic acid, may be regarded as acid and normal sulphides :—



**Behavior on Ignition.** Out of contact with the air, most sulphides remain unchanged. The sulphides of arsenic and mercury when heated sublime unchanged. Tin disulphide and iron disulphide give off part of their sulphur. All sulphides on being heated in contact with air (roasted) are oxidized either to oxides or to sulphates.

**Solubilities.** The sulphides of the alkalies are soluble in water; those of the alkaline earths, aluminum and chromium, are hydrolyzed by water with the formation of hydroxides; all other normal sulphides are insoluble in water.

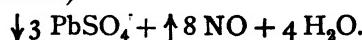
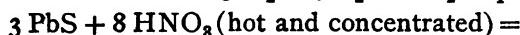
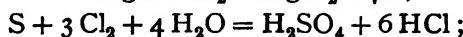
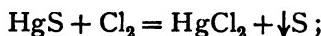
1. **Hydrochloric Acid**, when moderately strong (1 : 1), decomposes nearly all sulphides with the evolution of  $H_2S$ ; the latter may be recognized by its odor and by its property of turning lead acetate paper black:—



The few sulphides undecomposed by HCl are attacked by a mixture of zinc and HCl with the liberation of  $H_2S$ .

2. **Silver Nitrate** precipitates from solutions of sulphides or hydrogen sulphide, black silver sulphide ( $Ag_2S$ ), insoluble in cold but soluble in hot dilute nitric acid; it is insoluble in ammonium hydroxide.

3. **Oxidizing Solvents**, such as concentrated  $HNO_3$ , *aqua regia*,  $HCl + KClO_3$ , when used to dissolve a sulphide, do not liberate hydrogen sulphide, but cause a partial separation of sulphur and a partial oxidation of the sulphide to sulphuric acid:—



4. **Sodium Nitroprusside** [ $Na_2(NO)Fe(CN)_5$ ] imparts to normal alkali sulphide solutions a reddish purple color. An aqueous solution of  $H_2S$  does not give this reaction.

5. **Sodium Plumbeite** (prepared by adding caustic soda solution in excess to a lead salt) will detect a sulphide even in the presence of free alkali or carbonate, by producing a brown or black precipitate. This test is exceedingly sensitive.

6. For the oxidizing effect of the halogens, nitric acid, potassium dichromate, potassium permanganate, ferric salts, etc., on  $H_2S$ , see page 61.

**Insoluble Sulphides.** Sulphides insoluble in acids, when fused in a small nickel crucible with sodium hydroxide, are decomposed with the formation of sodium sulphide. If the mass is placed on a silver coin and then moistened, a black stain of silver sulphide ( $Ag_2S$ ) will be produced.

## NITRITES

**Solubilities.** Most nitrites are soluble in water; silver nitrite, however, is only sparingly soluble in water. On ignition, nitrites undergo decomposition with the production in general of nitrogen oxides and the oxide of the metal.

1. **Sulphuric Acid**, when dilute, decomposes all nitrites (distinction from nitrates) with the evolution of nitric oxide ( $\text{NO}$ ): the latter immediately oxidizes in contact with the air to brown nitrogen peroxide ( $\text{NO}_2$ ) \* :—

- (1)  $\text{NaNO}_2 + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{HNO}_2$ ;
- (2)  $3 \text{HNO}_2 = \text{HNO}_3 + \uparrow 2 \text{NO} + \text{H}_2\text{O}$ ;
- (3)  $\text{NO} + \text{O} = \text{NO}_2$ .

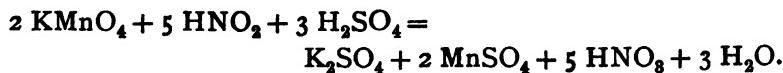
Nitrites are also decomposed by acetic acid with gentle heating; the  $\text{NO}_2$  given off may be recognized by its turning starch-iodide paper blue.

2. **Silver Nitrate** precipitates, from solutions of nitrites which are not too dilute, white silver nitrite ( $\text{AgNO}_2$ ), difficultly soluble in cold but more easily soluble in hot water.

3. **Cobalt Salts** solutions acidified with acetic acid give, with moderately strong solutions of potassium nitrite, a yellow precipitate of potassium cobaltic nitrite [ $\text{K}_3\text{Co}(\text{NO}_2)_6$ ].

4. **Potassium Iodide**, when added to a solution of a nitrite, and the mixture is acidified with acetic acid, produces a separation of iodine; the latter may be recognized by turning starch paste blue, or by coloring a drop of  $\text{CS}_2$  or  $\text{CHCl}_3$  violet.

5. **Potassium Permanganate** solution, when warmed, is bleached by a solution of a nitrite slightly acid with dilute sulphuric acid:—



\* The older nomenclature is applied to the oxides of nitrogen as being more distinctive.

### GROUP III

The acids of this group are not precipitated by either  $\text{AgNO}_3$  or  $\text{BaCl}_2$ .

#### ACETATES

**Solubilities.** All normal acetates are readily soluble in water. Some basic acetates, such as those of iron-(ic), aluminum, and chromium, are practically insoluble, while the normal silver and mercurous salts are only sparingly soluble. On ignition, acetates decompose with little or no charring and with the production of a combustible gas.

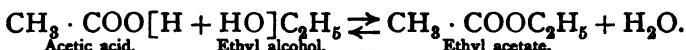
The alkali acetates, on ignition, are converted into carbonate and acetone :—



All other acetates behave similarly. If the carbonate is unstable at the ignition temperature, the oxide is produced ; if the latter is unstable, then the metal alone is left as a residue.

1. **Sulphuric Acid**, whether dilute or concentrated, liberates acetic acid from its salts ; the acid, being volatile, is easily recognized by its characteristic odor.

2. **Alcohol and Concentrated Sulphuric Acid.** If to a cooled mixture of an acetate and concentrated sulphuric acid, a little ethyl alcohol is added and then the mixture is gently heated, ethyl acetate will be formed ; the latter is easily recognized by its fruity odor. If amyl alcohol is used instead of ethyl alcohol, amyl acetate, having an odor resembling pear essence, will be produced :—



The reversible reaction is made to proceed almost entirely from left to right by the presence of the concentrated sulphuric acid, which removes the water as soon as it is formed.

3. **Silver Nitrate** gives with moderately concentrated solutions of an acetate or acetic acid a white crystalline precipitate of silver acetate ( $\text{AgC}_2\text{H}_5\text{O}_2$ ), sparingly soluble in cold water (1.04

parts of the salt dissolve in 100 parts of water at 20° C.), more readily soluble in hot water, and easily soluble in ammonium hydroxide.

4. **Ferric Chloride**, when added to an alkali acetate solution, produces a reddish brown solution, due to the formation of ferric acetate. If this solution is largely diluted and boiled, all of the iron will be precipitated as a basic ferric acetate :—



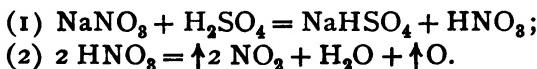
### NITRATES

**Solubilities.** The nitrates, with the exception of a few basic nitrates, such as  $\text{BiONO}_3$ , are all soluble in water. Barium nitrate, however, is only sparingly soluble in water and is almost insoluble in moderately strong nitric acid. All nitrates on ignition undergo decomposition, the alkali and alkaline earth nitrates yielding nitrites with the evolution of oxygen :—



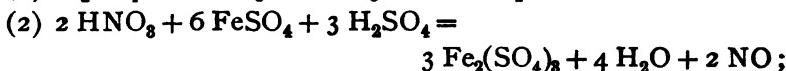
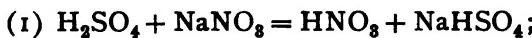
At higher temperatures, the nitrites are decomposed with the production of the oxides of nitrogen and a residue consisting of the oxide or peroxide of the metal. The nitrates of the heavy metals yield at a red heat nitrogen peroxide and oxygen. Heated on charcoal, all normal nitrates deflagrate.

1. **Concentrated Sulphuric Acid**, when added to a solid nitrate, causes the evolution of nitric acid. If the mixture is heated, the nitric acid is decomposed with the production of brown fumes of nitrogen peroxide ( $\text{NO}_2$ ) :—



2. **Ferrous Sulphate**, when added to a cool mixture of a nitrate solution and concentrated sulphuric acid, produces a deep brown color. The reaction may be considered as taking place in three stages: 1st, the liberation of nitric acid by the action of concentrated sulphuric acid on the nitrate; 2nd, the reduction of the free nitric acid by the ferrous sulphate, resulting in the production of nitric oxide; and, 3rd, the solution of the nitric oxide

in the excess of unoxidized  $\text{FeSO}_4$  with the formation of a brown unstable compound :—

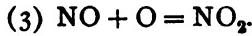
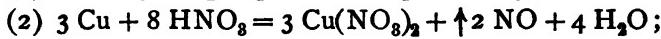
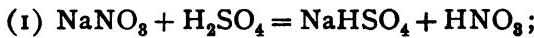


This test, which is exceedingly delicate, is carried out as follows : To about 3 cc. of the nitrate solution contained in a test tube, add an equal volume of concentrated sulphuric acid, mix, and *thoroughly* cool under running water. Hold the tube in an inclined position and cautiously add a few cc. of a strong, freshly prepared ferrous sulphate solution (free from nitrates), and allow the tube to stand. If a nitrate is present, a brown coloration will be produced in the zone of contact of the two liquids.

Nitrites give the same reaction, but may be carried out with dilute instead of concentrated sulphuric acid. The colored compound is destroyed on warming.

**3. Indigo Solution.** If to a little HCl that has been recently boiled, a few drops of a solution of indigo in sulphuric acid are added, and the mixture is then boiled, the blue coloration will persist, if the HCl contains no free chlorine. If to the blue solution a nitrate in the form of a solid or in solution is added, and the liquid is boiled, the indigo will be bleached. As the bleaching of the indigo is caused by the chlorine which is liberated, any other oxidizing agent, which will yield chlorine with HCl like  $\text{KClO}_3$ , will produce the same result.

**4. Copper Filings**, when added to a nitrate, and the mixture is heated with concentrated sulphuric acid, cause the production of brown nitrogen peroxide fumes :—



**5. Reduction to Ammonia.** If a solution of a nitrate is made strongly alkaline with  $\text{NaOH}$ , and a few pieces of aluminum or

zinc and iron filings are added, and the mixture is heated, ammonia gas will be evolved. Nitrites give the same reaction.

6. Free Nitric Acid may be recognized even in the presence of nitrates by adding to the solution a few quill cuttings and evaporating to dryness on the water bath. The quills will be found to have a yellow color, due to the formation of xanthoproteic acid; the same compound is formed when concentrated nitric acid is brought in contact with the skin.

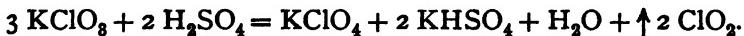
### CHLORATES

The chlorates are all soluble in water. On prolonged ignition, they are decomposed, giving off oxygen and leaving a residue of the chloride of the metal:—



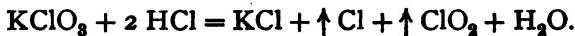
In consequence of the readiness with which they decompose with the liberation of oxygen, chlorates are valuable oxidizing agents. When they are mixed with organic matter and heated, deflagration results.

1. Concentrated Sulphuric Acid decomposes chlorates with the production of chlorine peroxide ( $\text{ClO}_2$ ), a very unstable, greenish yellow gas, which, on being warmed, violently explodes. The sulphuric acid acquires at the same time a deep yellow color, due to dissolved  $\text{ClO}_2$ :—



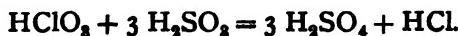
In carrying out the test, it is preferable first to warm a little concentrated sulphuric acid in a test tube and then to drop in a *very small* crystal of  $\text{KClO}_3$ . One should never look down into a test tube, especially when performing this test. Equal consideration is due one's neighbor.

2. Concentrated HCl, when added to a chlorate, is oxidized with the production of chlorine and chlorine peroxide:—



**3. Aniline Sulphate.** If to a solution of a chlorate in concentrated sulphuric acid a drop of aniline sulphate solution is added, a deep blue coloration will be developed; the color may be intensified by the addition of a few drops of water. This reaction is exceedingly delicate and may be used to distinguish a chlorate from a nitrate.

**4. Reducing Agents,** as sulphurous acid or the alkali sulphites in acid solutions, change the chlorates to chlorides:—



## ACID ANALYSIS

### *Preliminary Examination*

Before proceeding with the analysis for the acids, the student should first complete his examination for metals, the results of which will, by a proper use of the table of solubilities, restrict the number of acids to be looked for. An example will make this clear. If the substance under examination is soluble in water and lead has been found, none of the acids which form insoluble salts with lead need be looked for, viz., carbonic, sulphuric, hydrogen sulphide, chromic, oxalic, etc. Again, if the original substance is insoluble in water, but soluble in hydrochloric acid, and barium has been found, one need not look for sulphuric acid. Further, if silver has been detected in the metallic analysis of a substance soluble in water, it is evident that all the acids of Group II. need not be looked for. It is also well to remember that certain acids cannot coexist in solution, e.g., oxidizing agents like  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{H}_3\text{AsO}_4$ ,  $\text{FeCl}_3$  cannot exist with reducing agents like sulphites and iodides. It is also desirable that the first three of the following preliminary tests be carried out before commencing the systematic search for acids.

## PRELIMINARY TESTING OF SOLIDS

1. Heat a small quantity of the substance in a tube closed at one end.

OBSERVATION	INDICATION
<b>Decrepitation.</b>	NaCl, Pb(NO <sub>3</sub> ) <sub>2</sub> , K <sub>2</sub> SO <sub>4</sub> , zinc blende, and other substances.
<b>Carbonization, accompanied by burnt odor and formation of water.</b>	Organic matter, tartrates, and other organic acids and salts.
<b>Water given off.</b>	Water mechanically inclosed, water of hydration, and hydroxide.
<b>Gases given off :—</b>	
<b>Colorless and odorless.</b>	O—kindles a spark ; CO—burns with blue flame ; CO <sub>2</sub> —turns limewater turbid.
	NH <sub>3</sub> —turns red litmus blue ; SO <sub>2</sub> —recognized by odor ;
<b>Colorless with odor.</b>	(CN) <sub>2</sub> — recognized by odor,* and burns with reddish flame ; H <sub>2</sub> S—recognized by odor ; Acetone—recognized by odor.
<b>Colored gases.</b>	NO <sub>2</sub> —reddish brown ; turns starch-KI paper blue. Cl, Br, I—recognized by color and odor.
<b>A sublimate forms :—</b>	
<b>White.</b>	NH <sub>4</sub> salts, HgCl, HgCl <sub>2</sub> , As <sub>2</sub> O <sub>3</sub> , Sb <sub>2</sub> O <sub>3</sub> , and certain organic compounds.
<b>Yellow.</b>	As <sub>2</sub> S <sub>3</sub> , HgO (accompanied by globules of Hg).

\* Smell cautiously.

OBSERVATION	INDICATION
Yellow, becoming red when rubbed.	HgI <sub>2</sub> .
Reddish brown drops, yellow when cold.	S.
Black accompanied by garlic odor.	As.
Black accompanied by violet vapor.	I.
Metallic globules or mirror.	Hg.
Substance changes color:—	
Becomes black.	Salts of Cu, Ni, Co, Mn.
Becomes dark red.	Salts of Fe.
Black (hot) and red (cold) accompanied by metallic globules.	Hg salts.
Dark red (hot), yellow (cold).	PbCrO <sub>4</sub> .
Yellow (hot), white (cold).	ZnO.

2. Put a small quantity of the substance in a test tube, add a little dilute HCl, and heat gently.

OBSERVATION	INDICATION
CO <sub>2</sub> : effervescence, turns limewater turbid.	Carbonates.
SO <sub>2</sub> : recognized by odor.	Sulphites.
SO <sub>2</sub> : accompanied by a separation of S.	Thiosulphates.
H <sub>2</sub> S : recognized by odor and by lead acetate paper.	Sulphides.
NO <sub>2</sub> : brown, turns starch-KI paper blue.	Nitrites.
HCN : recognized by odor.*	Cyanides.

3. Heat a small portion in a test tube with concentrated sulphuric acid.

OBSERVATION	INDICATION
Acid fumes are evolved which redden litmus.	Halogen acids from their salts.
Br, I, mixed with HBr, SO <sub>2</sub> , and perhaps H <sub>2</sub> S.	Iodides and bromides.

\* Smell cautiously by fanning vapor with hand towards nose.

OBSERVATION	INDICATION
Chlorine — bleaching litmus.	Chloride and oxidizing agent together.
$\text{CrO}_2\text{Cl}_3$ — (reddish brown).	Chromate and chloride together.
$\text{ClO}_3$ — yellow color of gas and $\text{H}_2\text{SO}_4$ ; gas explosive.	Chlorate.
HF — etches glass ; yields $\text{SiF}_4$ , which turns "water bead" turbid.	Fluoride.
$\text{HC}_2\text{H}_3\text{O}_2$ — recognized by odor.	Acetate.
$\text{NO}_2$ — recognized by odor and by turning starch-KI paper blue.	Nitrates, nitrites.
$\text{SO}_2$ — recognized by odor.	Sulphite, thiosulphate, or reducing agent acting on $\text{H}_2\text{SO}_4$ .
$\text{SO}_2$ — accompanied by blackening.	Organic matter or tartrate.
CO — (without blackening) recognized by burning with blue flame.	Oxalate, cyanides, ferro- and ferricyanides.
$\text{CO}_2$ — turns limewater turbid.	Carbonates and oxalates.

#### 4. Heat alone on charcoal with blowpipe.

OBSERVATION	INDICATION
(a) Substance fuses and runs into charcoal.	Salts of Na, K, and Li.
(b) Substance decrepitates.	$\text{NaCl}$ and other compounds.
(c) Substance deflagrates.	Chlorates, nitrates.
(d) Substance is infusible; residue moistened with water reacts alkaline. Residue moistened with two drops of very dilute $\text{Co}(\text{NO}_3)_2$ solution and heated again gives a blue mass, green mass, pink mass.	Ba, Sr, Ca, Mg.  Al. Zn. Mg.
(e) Produces an incrustation that is white accompanied by garlic odor. Yellow (hot), white (cold). Yellowish brown (hot), white (cold), near residue, and not volatile. Reddish yellow (hot), yellow (cold). Orange (hot), light yellow (cold). Reddish brown, cold and hot.	As. Zn.  Sn. Pb. Bi. Cd.

5. Mix with anhydrous sodium carbonate and heat on charcoal.

OBSERVATION	INDICATION
(a) Metallic globule forms without incrustation :— yellow, red, white and malleable.	Au. Cu. Ag.
(b) Metallic globule with incrustation :— malleable, brittle.	Pb, Sn. Sb, Bi.
(c) Dark and brittle magnetic mass.	Fe, Co, Ni.

6. Make borax bead test; introduce first in oxidizing and then in reducing flame.

OXIDIZING FLAME	REDUCING FLAME	INDICATION
Blue.	blue.	Co.
Greenish blue.	red — opaque.	Cu.
Green.	green.	Cr.
Yellow.	green.	Fe.
Brown.	gray — opaque.	Ni.
Violet.	colorless.	Mn.

7. Moisten substance with concentrated HCl, take up a small portion on the loop of a platinum wire, and hold in the flame.\*

OBSERVATION	INDICATION
Intense yellow which persists for several seconds.	Na.
Deep red.	Li or Sr.
Reddish yellow.	Ca.
Green or greenish yellow.	Ba, Cu, or $H_3BO_4$ .
Pale blue.	As.

\* Certain substances, like the sulphates of the alkaline earths, are not volatilized in the flame; in such cases, it is well to hold them first in the reducing flame, then moisten with HCl, and introduce into the colorless bunsen flame.

### Method of Acid Analysis

The method employed for the detection of the acids is different from that used in the systematic examination for metallic radicals. We cannot, as was done with the metals, divide the acids into groups by certain reagents and then separate the various group precipitates into their component acids. For the most part, the procedure consists in independently and separately testing for each of them. From the list of acids this would seem a long and tiresome task, but in actual practice the number of acids which must be looked for is very much reduced; first, from a knowledge of the solubilities and metallic content of the substance; and, second, by the results furnished by the preliminary experiments just given. The reagents  $\text{BaCl}_2$  and  $\text{AgNO}_3$ , when properly applied, are valuable in that they give indications of the presence or absence of whole groups; e.g., if to a moderately concentrated and neutral solution of the substance,  $\text{BaCl}_2$  or  $\text{CaCl}_2$  is added and no precipitate results, the absence of all the members of Group I. may be inferred.\* However, these reagents cannot be used to separate the acids in the manner in which group reagents are employed to precipitate metallic groups.

### GENERAL EXAMINATION FOR ACIDS

Preliminary treatment of the sample with dilute HCl will disclose the presence or absence of the following acids:  $\text{H}_2\text{CO}_3$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{S}_2\text{O}_3$ ,  $\text{H}_2\text{S}$ , HCN, and  $\text{HNO}_2$ . In the course of the analysis for metals,  $\text{H}_3\text{AsO}_3$ ,  $\text{H}_3\text{AsO}_4$ , and  $\text{H}_2\text{CrO}_4$  will be detected. For the examination for acids, it is desirable in most cases to have a solution which shall contain the acids in the form of sodium salts. Such a solution, known as the "prepared solution," may be obtained by boiling the finely powdered substance with an excess of  $\text{Na}_2\text{CO}_3$  solution, with constant stirring, for several minutes (1). If ammonia is given off, boil with the addition of more  $\text{Na}_2\text{CO}_3$  until no more of this gas is evolved, and then filter.

\* The solution should also contain no considerable quantity of  $\text{NH}_4$  salts, else borates, fluorides, and tartrates may not precipitate.

Residue will contain the hydroxides, carbonates, and basic carbonates of the metals (except the alkalies, As and Sb); it may also contain phosphates, fluorides, and silicates. Reserve this residue, and if these acids are *not* found in the filtrate, divide it into two parts.

1st part. Test for  $H_3PO_4$  and  $SiO_2$ .

Acidify with  $HNO_3$ , evaporate to dryness, extract with hot dil.  $HNO_3$ , and filter. Test residue with  $NaPO_3$  bead or with HF in a platinum crucible. Test filtrate for  $PO_4$  with  $(NH_4)_2MoO_4$ .

2nd part. Test for HF.

Filtrate (prepared solution) will contain the acids in form of sodium salts + an excess of  $Na_2CO_3$  and is to be used for the acid tests unless otherwise directed.

#### Preliminary Tests for the Acid Groups

*Just* acidify a *small portion* of the prepared solution by the careful addition of dil.  $HNO_3$ ; filter if necessary (2) and boil the filtrate until all of the  $CO_2$  is expelled. Render faintly alkaline with ammonia, and boil off any excess of the latter that may have been added; filter again if necessary. Divide this solution into 2 parts.

1st part. Test for Group I. by adding a little  $BaCl_2$  and  $CaCl_2$  solutions (3). A white precipitate shows the presence of the Group I. (4); acidify with HCl. If the ppt. does not dissolve,  $H_2SO_4$  is present. If the group is present, test separate portions of the prepared solutions for  $H_3PO_4$ ,  $H_3BO_3$ , HF,  $H_2C_2O_4$ ,  $H_2C_4H_4O_6$ ,  $H_2SiO_3$ .

2nd part. Test for Group II. Render the solution acid with  $HNO_3$  and add an *excess* of silver nitrate. A ppt. proves the presence of Group II. Note the color of the ppt. (5) and filter.

Residue. Wash several times on filter with water. Transfer ppt. to a test tube and shake vigorously with an excess of dilute  $NH_4OH$ . If complete solution takes place, the absence of HI and  $H_4Fe(CN)_6$  is shown. HBr and HCNS may also possibly be absent. If Group II. is shown to be present, test separate portions of the prepared solutions for HI, HBr,  $HCl$ , HCN,  $H_4Fe(CN)_6$ ,  $H_3Fe(CN)_6$ , and HCNS.

To filtrate or solution in which  $AgNO_3$  produces no ppt. in  $HNO_3$  solution, add more  $AgNO_3$  to insure complete precipitation; filter if necessary, and to the filtrate contained in a test tube carefully add 3 to 5 drops of ammonia. Agitate the upper portion of the liquid and note the color of any ppt. which may form at the neutral zone (6).

Group III. Test separate portions for  $HClO_3$ ,  $HNO_3$ , and  $HC_2H_3O_2$ .

## NOTES

**1.** If the substance is soluble in water and contains no heavy metals, the treatment with  $\text{Na}_2\text{CO}_3$  may be dispensed with. If acid (preferably nitric acid) has been used in getting the substance into solution, and the latter is boiled,  $\text{H}_2\text{CO}_3$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{S}_2\text{O}_3$ ,  $\text{H}_2\text{S}$ , HCN, and  $\text{HC}_3\text{H}_4\text{O}_2$  will be driven off or decomposed, and therefore should not be looked for; the presence of all of these acids will have been revealed, however, in the preliminary examination. Substances insoluble in water but soluble in acids, when boiled with  $\text{Na}_2\text{CO}_3$  solution, may leave a residue consisting of the phosphates and fluorides of certain metals which are not readily transposed by boiling with  $\text{Na}_2\text{CO}_3$ . Substances insoluble in acids should be fused in a platinum crucible if no reducible metals are present, otherwise in either a nickel or a porcelain crucible with  $\text{Na}_2\text{CO}_3$ ; the melt is then extracted with boiling water and the solution is filtered. The filtrate will correspond to the "prepared solution" and should be used for the acid tests. The residue is tested for phosphates and fluorides. In certain cases where As and Sb are known to be present, it may be necessary to remove these metals by passing  $\text{H}_2\text{S}$  into the acidified solution, filtering, and boiling out the  $\text{H}_2\text{S}$  from the filtrate. The latter may then be treated with  $\text{Na}_2\text{CO}_3$  in the manner already described. In the absence of nitrates and chlorates and in the presence of only metals which are precipitated by  $\text{H}_2\text{S}$ , a solution for the acid tests may be prepared by saturating with  $\text{H}_2\text{S}$  a suspension of about 1 g. of the substance in about 50 cc. of water. Heat to boiling and filter. The filtrate after boiling to expel the  $\text{H}_2\text{S}$  is used in small portions for the acid tests. Nitrates and chlorates, if present, would oxidize the  $\text{H}_2\text{S}$ , forming  $\text{H}_2\text{SO}_4$ ; while chlorates would be reduced to chlorides, thus making the tests for these acids of no value.

**2.** Boiling with  $\text{Na}_2\text{CO}_3$  will leave all of the metals in the residue, with the exception of the alkalies, As, Sb, and small amounts of metals slightly soluble in excess of  $\text{Na}_2\text{CO}_3$ . On acidifying this solution, a precipitate may be obtained. It should be filtered off, rejected, and the filtrate again boiled to drive out any  $\text{H}_2\text{S}$  that may be liberated before neutralizing the solution with ammonium hydroxide. All the  $\text{CO}_2$  must be expelled after acidifying, otherwise  $\text{BaCO}_3$  and  $\text{Ag}_2\text{CO}_3$  will precipitate when the group reagents are added. Too much  $\text{HNO}_3$  should be avoided, as this will form with the ammonia next to be added an unnecessarily large amount of  $\text{NH}_4\text{NO}_3$ , in which the Ca or Ba salts of nearly all the acids of Group I., especially the borate, fluoride, and tartrate, are soluble.

**3.**  $\text{CaCl}_2$  is also added because the fluoride, tartrate, and oxalate of calcium are much more insoluble than the corresponding salts of Ba.

**4.** If no precipitate is obtained, the absence of all the acids of Group I. is proved with the exception of boric acid, which is precipitated only from rather concentrated solutions. It should, however, be remembered that the presence

of much ammonium salts interferes more or less with the precipitation of all the acids of this group with the exception of  $H_2SO_4$  and  $H_2C_2O_4$ .

5. If only a cloudiness is obtained with  $AgNO_3$ , it indicates a trace of chlorides which should not be reported.  $Ag_2C_2O_4$  is difficultly soluble in  $HNO_3$ ; an excess of this acid should be added before adding the  $AgNO_3$  to prevent its precipitation. The color of the silver precipitate, together with its solubility in ammonium hydroxide, affords important indications of the acid present:  $AgI$  is yellow;  $Ag_2S$ , black;  $Ag_2Fe(CN)_6$ , reddish brown;  $AgCl$ ,  $AgCN$ ,  $AgSCN$ , and  $Ag_4Fe(CN)_6$  are white; and  $AgBr$  is yellowish white. Of these, only the sulphide, iodide, and ferrocyanide are insoluble in ammonium hydroxide; the bromide and thiocyanate are difficultly soluble in this reagent.

6. Silver nitrate also precipitates from *neutral* solutions all the acids of Group I. with the exception of HF and  $H_2SO_4$ ; the latter is, however, difficultly soluble in water. The color of the precipitate forming at the neutral junction of the two liquids will often indicate which of the acids of Group I. are present; if yellow, it may be  $Ag_3PO_4$  or  $Ag_3AsO_3$ ; if brownish red,  $Ag_3AsO_4$ ; if purplish red,  $Ag_2CrO_4$ ; if white, the oxalate, silicate, or borate.

### SPECIAL TESTS FOR THE ACIDS

The metallic analysis and preliminary tests completed, the student should, with the aid of the table of solubilities, thoughtfully prepare a list of acids which are likely to be present and hence to be looked for. No acid should be excluded which is compatible with the solubility and metallic content of the substance. Minerals, as a rule, need not be tested for organic and cyanogen acids, and, if insoluble, for nitrates, chlorates, bromides, and iodides. Alloys contain no acids as such; they may, however, contain acid-forming elements such as S, P, and Si, which, by treatment with suitable oxidizing agents, will yield the corresponding acids.

### CARBONATES

Treat a small portion of the finely ground substance in a test tube with dilute HCl and warm. A carbonate, if present, will evolve  $CO_2$ , which may be recognized by its property of rendering turbid a drop of limewater supported in a glass tube.

## NOTES

1. Sulphites, if present, would evolve  $\text{SO}_2$ , which would also render lime-water turbid. Sulphides and nitrites also liberate gases on treatment with dilute HCl. To avoid the interference of these substances, use a strong solution of  $\text{K}_2\text{Cr}_2\text{O}_7$ , instead of acid, and warm the mixture.  $\text{CO}_2$  alone will be evolved.  $\text{K}_2\text{Cr}_2\text{O}_7$  oxidizes sulphides and sulphites, and is without action on nitrites. The same end may be attained by treatment with acid and then passing the evolved mixed gases through bromine water.
2. Certain carbonates are not readily decomposed by cold dilute acid, e.g., magnesite, dolomite, and the carbonates of the heavy metals. They are all decomposed, however, on warming the acid.
3. In making the test, care must be exercised to prevent any acid, which may be mechanically carried up the tube in the form of spray, from coming in contact with the drop of limewater.
4. The drop of limewater should be examined *shortly* after exposure to insure the non-formation of soluble calcium dicarbonate.
5. Where the amount of  $\text{CO}_2$  liberated is small, it is necessary to heat the acid to drive out the  $\text{CO}_2$ , which otherwise would remain wholly in solution and thus escape detection.

## SULPHITES

Treat a small quantity of the solid substance with dilute HCl. In the presence of a sulphite,  $\text{SO}_2$  will be evolved; this gas may be readily recognized by its odor and by its property of bleaching a very dilute solution of  $\text{KMnO}_4$  (see reaction 6 under *Sulphites*).

## THIOSULPHATES

These are detected in the preliminary tests with dilute HCl. In the presence of a thiosulphate,  $\text{SO}_2$  is evolved, accompanied by a separation of S.

## SULPHATES

Sulphates will have been indicated in the preliminary testing for the groups of acids. To a small portion of the "prepared solution," add dilute HCl to acid reaction, boil to expel  $\text{CO}_2$ , filter if necessary, and to the filtrate add  $\text{BaCl}_2$ . A white precipitate indicates the presence of sulphates or fluosilicates. To confirm the presence of sulphates, dry the precipitate, mix it with a little anhydrous  $\text{Na}_2\text{CO}_3$ , and heat on charcoal before

the blowpipe. Remove the residue from the charcoal, place it on a bright silver coin, and add a drop of water. A black stain confirms the presence of a sulphate.

### FLUOSILICATES

Acidify a small portion of the prepared solution with dilute HCl, boil out the CO<sub>2</sub>, filter if necessary, and to the clear filtrate add BaCl<sub>2</sub> to complete precipitation. Allow to stand for several minutes and filter. Wash and completely dry the precipitate at a low temperature. Transfer the precipitate to a test tube, add concentrated H<sub>2</sub>SO<sub>4</sub>, heat, and hold in the escaping gases a drop of water held on the loop of a platinum wire. In the presence of a fluosilicate, the drop of water will become turbid owing to the formation of H<sub>4</sub>SiO<sub>4</sub>. (See footnote, page 124.)

### CHROMATES

(a) Solutions of a dichromate or a chromate possess an orange or yellow color which is very characteristic. Acidification with dilute HCl, followed by treatment with H<sub>2</sub>S, will cause a change in color to green, accompanied by a separation of S; hence this acid will be detected in the precipitation of the second group of metals. The presence of a chromate may be detected by acidifying the prepared solution with HNO<sub>3</sub>, thoroughly cooling, and then adding 1 cc. of ether and 1 cc. of 3% H<sub>2</sub>O<sub>2</sub> and shaking. A blue color in the ether layer proves the presence of a chromate. Reaction 6, page 143.

(b) The change in color, which is an evidence of reduction, may be brought about by a variety of reducing agents in the presence of free acid, e.g., strong HCl and a little alcohol (see reaction 5 under *Chromates*), KI, and Na<sub>2</sub>SO<sub>3</sub>; the last is oxidized at the same time to sulphate. If the prepared solution is colorless, chromates cannot be present.

(c) Precipitation Test. In the absence of sulphates, phosphates, oxalates, and tartrates, acidify the "prepared solution" with acetic acid, boil to expel CO<sub>2</sub>, filter if necessary, and to the clear solution add 1 g. of NaC<sub>2</sub>H<sub>8</sub>O<sub>2</sub> and a little Pb(C<sub>2</sub>H<sub>8</sub>O<sub>2</sub>)<sub>2</sub>.

solution. A yellow precipitate of  $PbCrO_4$  proves the presence of a chromate.

If the above-mentioned acids are present, acidify the prepared solution with  $HNO_3$ , boil to expel  $CO_2$ , filter if necessary, and render the resulting filtrate just alkaline with ammonium hydroxide; add  $CaCl_2$ , warm, shake vigorously, and allow to stand half an hour and filter. The precipitate may consist of the tartrate, oxalate, and phosphate of calcium. The filtrate may contain sulphates besides the chromate. To remove the former, acidify with  $HNO_3$ , heat to boiling, add a slight excess of  $BaCl_2$ , and filter off the  $BaSO_4$  on two folds of filter paper. To the filtrate add several grams of  $NaC_2H_5O_2$  to completely replace the nitric acid by acetic acid, and heat, when a yellow precipitate of  $BaCrO_4$  will be formed.

#### ARSENITES

Arsenites are detected in the analysis for metals. In  $HCl$  solutions,  $H_2S$  yields an immediate precipitate of  $As_2S_3$ . Arsenites are not precipitated by either magnesia mixture or ammonium molybdate. In a strictly neutral solution,  $AgNO_3$  produces a yellow precipitate of  $Ag_3AsO_3$  (phosphates respond to the same test).

#### ARSENATES

From acid solutions,  $H_2S$  slowly yields a yellow precipitate. From strictly neutral solutions,  $AgNO_3$  precipitates reddish brown  $Ag_3AsO_4$ . Precipitates are obtained with both magnesia mixture and ammonium molybdate. The last two tests apply only in the absence of phosphates. For distinctions between phosphates and arsenates, see reactions 4 and 5 under *Phosphates*. If arsenic is found in the metallic analysis, it is usually present as arsenite or arsenate. In the absence of oxidizing agents, as chromic and nitrous acids, arsenates are further distinguished from arsenites, even in the presence of phosphates, by the ability of arsenates to liberate iodine from  $KI$  in a solution acid with  $HCl$ . For the detection of *Iodine*, see p. 147.

### PHOSPHATES

Phosphates will have been detected in a complete analysis before precipitating the third group of metals.

(a) In the absence of arsenates, a small portion of the prepared solution is strongly acidified with concentrated  $\text{HNO}_3$ , then it is evaporated nearly to dryness, diluted with water, treated with 10 cc. of ammonium molybdate solution, and warmed; in the presence of a phosphate, a yellow precipitate of  $(\text{NH}_4)_8\text{PO}_4 \cdot 12 \text{MoO}_3$  will be formed.

(b) Or the prepared solution is acidified with HCl, boiled to expel  $\text{CO}_2$ , filtered if necessary, made alkaline with ammonium hydroxide, filtered again if a precipitate forms, and the clear, cooled filtrate is treated with magnesia mixture and thoroughly shaken. A white crystalline precipitate of  $\text{NH}_4\text{MgPO}_4$  forms in the presence of a phosphate.

### NOTES

1. The solution is evaporated with concentrated  $\text{HNO}_3$  to oxidize any reducing agent that may be present and which would interfere with the  $(\text{NH}_4)_8\text{MoO}_3$  test; it also converts at the same time any meta- or pyro-phosphate to the ortho form, which alone is precipitated by  $(\text{NH}_4)_8\text{MoO}_3$ .

2. If arsenic has been found, it should be removed by rendering the prepared solution strongly acid with HCl, heating to boiling, and passing in a stream of  $\text{H}_2\text{S}$  for 20 minutes; then filter, boil out the  $\text{H}_2\text{S}$  from the filtrate, add  $\text{HNO}_3$ , and evaporate nearly to dryness; extract the residue with boiling dilute  $\text{HNO}_3$  and add to the somewhat cooled solution an excess of ammonium molybdate. A yellow precipitate shows the presence of  $\text{PO}_4$ . The solution to be tested for  $\text{PO}_4$  should not be above 70° C., as there is danger of decomposing the reagent, with the resulting precipitation of white  $\text{MoO}_3$ .

### OXALATES

Oxalates should be detected before proceeding with the precipitation of Group III.

Slightly acidify some of the prepared solution with acetic acid, boil out the  $\text{CO}_2$ , and filter if necessary; warm the filtrate and add an equal volume of a saturated  $\text{CaSO}_4$  solution. A white crystalline precipitate indicates the presence of an oxalate.

Confirm by filtering off the precipitate, washing it with water, dissolving it in hot dilute  $H_2SO_4$ , and adding a drop of dilute  $KMnO_4$  solution. In the presence of an oxalate, the  $KMnO_4$  will be bleached. (See reaction 4 under *Oxalates*.)

#### NOTES

The solution is rendered acid with acetic acid to prevent the precipitation of carbonates and phosphates.  $CaF_2$  may be precipitated, but may usually be distinguished from  $CaC_2O_4$  by the fact that the former is gelatinous while the latter is crystalline. It is, however, better to make the confirmatory test.

#### FLUORIDES

1. The etching test (see page 133) is not applicable in the presence of silicates or silica.
2. The test depending upon the formation of  $SiF_4$  and the detection of the latter by its property of rendering a water "bead," held on the loop of a platinum wire, turbid (see page 132), is applicable to fluorides in the presence of  $SiO_2$  or silicates. To insure a positive test, a little sand or dry sodium silicate should be added.
3. Silicates which are not decomposed by concentrated  $H_2SO_4$  may be tested for fluorides by fusing with 6 to 8 times their weight of a mixture of equal parts of sodium carbonate and potassium carbonate, extracting the melt with water, and filtering. The filtrate will contain all of the F as  $NaF$ , as well as the silica in the form of  $Na_2SiO_3$ . Acidify with acetic acid and filter off any precipitate which forms. To the filtrate, add  $CaCl_2$  and allow the mixture to stand for some time. Collect the precipitate on a filter, dry, and apply the tests for a fluoride.

#### BORATES

1. Turmeric Paper Test. Dip a piece of turmeric paper into a small portion of the original or prepared solution acidified with  $HCl$  and dry it; this may be conveniently accomplished by placing it on the outside of a test tube containing water which has just been heated to boiling. In the presence of a

borate, the turmeric paper assumes a permanent reddish brown color, which, on treatment with a drop of caustic alkali, is changed to a greenish black color.

2. **The Flame Test** (see reactions 6 and 7 under *Borates*) may be conducted on a portion of the original substance, provided Ba and Cu are both absent. If these metals are present, the test may be applied by first removing the Cu with  $H_2S$  and then the Ba with sulphuric acid. If the test is carried out in a test tube provided with a stopper, through which passes a glass tube drawn out near the end, and the mixture is heated, only the vapors of boron ester will escape. If the issuing gas is lighted, it will burn with a green flame. The advantage of this form of apparatus is that, as neither Ba nor Cu form volatile compounds under these conditions, they do not interfere.

#### NOTES ON THE TURMERIC TEST

Oxidizing agents like chlorates, chromates, and iodides interfere with this test by destroying the turmeric.  $HNO_3$  is an exception. Chlorates and chromates may both be reduced by treating the original substance contained in an evaporating dish with solid  $Na_2SO_3$ , adding dilute HCl, and warming after the reaction has proceeded for some time, to drive out the excess of  $SO_3$ . Filter, if necessary, and boil the filtrate with a slight excess of  $Na_2CO_3$ ; dilute, and filter. Iodides, if present, may be removed by precipitation with  $AgNO_3$  after rendering the solution acid with  $HNO_3$ .  $FeCl_3$ , if present, will color the turmeric paper brown on concentration, but will give a brown instead of a greenish black color when the dried paper is treated with caustic soda. It is evident that if the prepared solution is used, Fe cannot be present.

#### SILICATES

1. The  $NaPO_3$  bead test may be applied to the original substance.

2. **Evolution of  $SiF_4$ .** In a platinum crucible, treat a mixture of equal parts of the dry substance and  $CaF_2$  (free from  $SiO_2$ ) with a little concentrated  $H_2SO_4$ , and heat under a hood. A drop of water, held on the loop of a platinum wire, when brought near the mouth of the crucible, will be rendered turbid by the escaping  $SiF_4$ . About 2 cc. of aqueous HF may be used instead of the  $CaF_2$ .

## TARTRATES

The presence of tartrates will be indicated when the substance under examination is heated in a closed tube, as well as by the characteristic behavior when heated with concentrated  $H_2SO_4$  (see reaction 1 under *Tartrates*).

1. Concentrate the prepared solution to about 0.5 cc., just acidify with acetic acid, and add 2 cc. of  $KC_2H_3O_2$ ; shake vigorously and allow the mixture to stand. A white crystalline precipitate may be  $KHC_4H_4O_6$ . Confirm by dissolving in a few drops of dilute KOH solution, and precipitate the tartrate with a little  $AgNO_3$ ; dissolve the precipitate in a slight excess of ammonium hydroxide and carry out the silver mirror test as described in reaction 2 under *Tartrates*.
2. If no heavy metals are present and the substance is soluble in water, the silver mirror test may at once be applied.
3. If heavy metals are present, dissolve the original substance in water or in the least possible amount of dilute HCl. Remove the metals of Groups I. and II., if present, by means of  $H_2S$ ; and those of Group III. with  $NH_4OH$  and  $(NH_4)_2S$  (Al and Cr will, of course, not be precipitated). The clear filtrate is acidified with HCl, boiled to expel  $H_2S$ , and is finally rendered alkaline with  $NH_4OH$ . An excess of  $CaCl_2$  is then added and the mixture is shaken vigorously, allowed to stand for a short time, and finally filtered. The precipitate, which may consist of  $CaC_4H_4O_6$ ,  $CaC_2O_4$ , and  $Ca_3(PO_4)_2$ , is treated with a cold, strong NaOH solution to dissolve out the  $CaC_4H_4O_6$ , then it is stirred thoroughly, diluted, and filtered. If a precipitate forms on heating the clear filtrate to boiling, a tartrate is indicated. Confirm by filtering while hot, wash the precipitate, and transfer it to a test tube. Add 1 drop of  $NH_4OH$  and a little  $AgNO_3$ , and warm. In the presence of a tartrate, a black precipitate or a silver mirror will be formed.

## GROUP II

## IODIDES

1. Iodides, if present, will be detected in the preliminary examination of the substance with concentrated  $H_2SO_4$ .
2. To a portion of the original or prepared solution acidified with HCl, add a little potassium nitrite solution or chlorine water and then about 1 cc. of  $CS_2$  or  $CHCl_3$ , and shake vigorously. An iodide, if present, will color the  $CS_2$  or  $CHCl_3$  violet.
3.  $AgNO_3$  in  $HNO_3$  solution precipitates yellow  $AgI$ , practically insoluble in  $NH_4OH$ .

## NOTES

Nitrous acid—*i.e.*, a nitrite in acid solution—is preferable to chlorine as an iodine liberator for the reason that an excess of the former does not hinder the reaction (see reaction 4 under *Iodides*). The liberated iodine may also be recognized by the blue compound it forms with starch paste. Insoluble iodides are tested for the halogen by one of the methods given under “*Insoluble Substances*,” page 195.

## BROMIDES

1. Bromides, if present, will be detected in the preliminary examination of the substance with concentrated  $H_2SO_4$ .
2. To a portion of the original or prepared solution, acid with HCl, add 1 cc. of  $CS_2$  or  $CHCl_3$ . Cautiously treat with small amounts of Cl water and shake vigorously after each addition. In the presence of bromides, the  $CHCl_3$  or the  $CS_2$  will acquire a reddish or yellow color, depending upon the amount of bromide present (see reaction 2 under *Bromides*).

## NOTES

Iodides, if present, interfere with the test by imparting a violet color to the  $CHCl_3$  or  $CS_2$ . If the amount of iodide present is large, chlorine water should be added until an intense violet color is produced in the  $CHCl_3$  or  $CS_2$ ; the liquid is then carefully decanted or the aqueous portion is removed to another test tube by means of a pipette, and there treated with fresh portions of  $CS_2$  and Cl water. If the  $CS_2$  is still colored a deep violet, the operation is repeated until only a faint pink color is imparted to the  $CS_2$ ; now, on adding a little more Cl water and shaking, a brown or reddish color will be produced if

a bromide is present. If the amount of iodide in the original solution is small, as is shown by the faint purple color of the  $\text{CS}_2$ , more chlorine water should be added, without decanting the liquid, and the mixture should be shaken after each small addition; in the presence of a bromide, a characteristic brown color will finally be observed in the  $\text{CS}_2$  layer. Chlorine water exercises a selective action, liberating practically all the iodine first; an excess will oxidize the latter to colorless iodic acid; and on further addition of chlorine water, bromine will be liberated. Insoluble bromides are treated as directed under "*Insoluble Substances*," page 195.

Thiocyanates, cyanides and ferrocyanides interfere with the detection of bromides by the chlorine water test for the reason that these acids are readily oxidized by the reagent added to liberate the Br. This difficulty may be overcome by the method devised by Curtman and Wickoff which is based on the fact that in a solution slightly acid with  $\text{H}_2\text{SO}_4$ , cuprous sulphate (prepared by adding  $\text{H}_2\text{SO}_4$  to  $\text{CuSO}_4$ ) precipitates cyanides, ferrocyanides, and thiocyanates (also iodides), leaving in solution bromides and chlorides.

**METHOD.** The solution to be tested, which should be neutral or slightly acid with  $\text{H}_2\text{SO}_4$ , is treated with 15 cc. saturated solution of  $\text{SO}_2$ . Heat to boiling and while hot add slowly 2 N —  $\text{CuSO}_4$  until an excess is added. The solution should be blue; a green color shows insufficient  $\text{CuSO}_4$ . Filter while hot and wash the ppt. twice with hot water, adding the washings to the filtrate. Boil down the filtrate to 5-10 cc. to concentrate the solution and to expel the excess  $\text{SO}_2$ . (A slight white ppt. which may separate should be discarded.) Transfer solution to a test tube and cool. Now add 1 cc. 3 N —  $\text{H}_2\text{SO}_4$  and 1 cc. 1%  $\text{KMnO}_4$  and shake. Add 0.5 cc.  $\text{CS}_2$  and shake again. A yellow color in the  $\text{CS}_2$  layer proves the presence of Br. The acid and  $\text{KMnO}_4$  are added and shaken first in order that the  $\text{CS}_2$  may not be in contact with the  $\text{KMnO}_4$  longer than is necessary, since they react with the formation of a little  $\text{MnO}_2$  which with vigorous shaking may dissolve in the  $\text{CS}_2$ , yielding a color indistinguishable from that given by small amounts of Br.

### CHLORIDES

In the absence of bromides, iodides, cyanides, ferrocyanides, and thiocyanates, a white precipitate, obtained with  $\text{AgNO}_3$  in a solution acid with  $\text{HNO}_3$ , is proof of the presence of chlorides.

Chlorides in the presence of iodides and absence of bromides, cyanides, and ferricyanides are tested as follows: To the  $\text{HNO}_3$  solution, add  $\text{AgNO}_3$  to complete precipitation, filter, and wash; digest the precipitate for several minutes with cold ammonium hydroxide and filter; finally acidify the filtrate with  $\text{HNO}_3$ , when

the formation of a white curdy precipitate shows the presence of a chloride.

**Chlorides in the presence of Bromides and Iodides** may be detected by one of three following methods:—

**1. The Chromyl Chloride Method.** In a small, *dry* distilling flask, place a mixture of some of the powdered original substance, or the residue obtained by the evaporation to dryness of a portion of the prepared solution, and powdered  $K_2Cr_2O_7$ ; add 5 cc. of concentrated  $H_2SO_4$ , and heat. Absorb any fumes that may be evolved in dilute  $NH_4OH$ . The latter will be colored yellow if a chloride was originally present (see reaction 4 under *Chlorides*).

**2. Hart's Method.** Principle:  $HI$  is oxidized by a ferric salt and the  $I$  set free is boiled off;  $HBr$  is then oxidized with  $KMnO_4$  and the liberated  $Br$  is removed by boiling; any residual substance which will give with  $AgNO_3$  a white precipitate insoluble in  $HNO_3$  and soluble in ammonium hydroxide, must be a chloride. The method is not reliable for the detection of very small amounts of chlorides in the presence of relatively large amounts of the others.

**METHOD.** The solution contained in an evaporating dish is rendered slightly acid with dilute  $H_2SO_4$ , then treated with a concentrated solution of ferric alum, and the mixture boiled until no more iodine is given off. This point may be determined by holding in the escaping vapors a piece of paper moistened with starch paste, which, in the presence of iodine, will be colored blue. When the expulsion of the iodine is complete,  $KMnO_4$  solution is added in a quantity sufficient to give the solution a purple color which does not disappear on boiling. The  $KMnO_4$  oxidizes the  $HBr$ , setting bromine free, and this halogen escapes with the steam. The boiling is continued until a piece of moistened starch-iodide paper, held in the vapor, is no longer turned blue, showing the absence of bromine. If the solution is now purple, showing an excess of  $KMnO_4$ , a few drops of alcohol are added, the mixture is boiled with stirring, and the brown hydrated  $MnO_2$  is filtered off. The filtrate, which should be colorless, is treated with a few drops of  $AgNO_3$ . A white precipitate, insoluble in  $HNO_3$  and soluble in ammonium hydroxide, proves the presence of a chloride.

**3. Vortmann's Method** consists in acidifying the prepared solution with acetic acid, adding  $PbO_2$ , and boiling until no more

bromine and iodine are given off (as shown by tests) and the solution on settling is colorless.

All the hydrobromic acid and part of the hydriodic acid are oxidized by the  $PbO_2$ ; the remainder of the iodine, combined in the form of lead iodide, settles on the bottom of the beaker along with the excess of  $PbO_2$  added. Filter and wash the precipitate with hot water, and test the filtrate for chlorides with  $AgNO_3$ .

#### NOTES

Cyanides, ferrocyanides, ferricyanides, and thiocyanates interfere with the tests for the halides; they must therefore be removed before the tests are applied. This is accomplished by completely precipitating both cyanides and halides with  $AgNO_3$ , then filtering, drying, separating the precipitate from the filter, and igniting in a dish or crucible. By this procedure, the cyanogen compounds are decomposed with the separation of Ag, while the silver halides remain unchanged. The latter are best got into solution by fusing them with  $Na_2CO_3$ , extracting the melt with water, and filtering. The filtrate will contain  $NaCl$ ,  $NaBr$ ,  $NaI$ , and an excess of  $Na_2CO_3$ . The solution is acidified with  $HNO_3$  and the tests for the halogen acids are made as given above. Or the residual silver halides may be treated with Zn and dilute sulphuric acid, and the action allowed to continue for half an hour. The halogens go into solution as Zn salts, and, after filtering, the filtrate is tested for the halogen acids as given above.

#### FERROCYANIDES

A small portion of the prepared solution is acidified with HCl and a little  $FeCl_3$  is then added. In the presence of a ferrocyanide, a blue precipitate of prussian blue is obtained.

#### FERRICYANIDES

1. To a small portion of the prepared solution acidified with HCl, add a freshly prepared solution of  $FeSO_4$ ; the formation of a dark blue precipitate of Turnbull's blue proves the presence of a ferricyanide.

2. From a nitric acid solution,  $AgNO_3$  precipitates reddish brown  $Ag_3Fe(CN)_6$ .

#### THIOCYANATES

1. Acidify a portion of the prepared solution with HCl and add  $FeCl_3$ ; a deep red coloration, due to the formation of

ferric thiocyanate, proves the presence of a thiocyanate. The solution is acidified with HCl to prevent the interference of (1) acetic acid, which, with  $\text{FeCl}_3$ , would give a red coloration owing to the formation of ferric acetate; and (2) to prevent tartaric acid and other hydroxy-acids from combining with  $\text{FeCl}_3$ .

#### NOTES

Ferri- and ferro-cyanides interfere by yielding precipitates or blue solutions which may completely mask the red color due to HCNS. Iodine, set free by oxidizing agents which may be present, also interferes with this test by the color it imparts to the solution. All these interfering substances may be removed by distilling the HCNS. This is accomplished by adding to a portion of the prepared solution acidified with HCl a little  $\text{SnCl}_4$  sufficient in amount to reduce any I or Br present to their corresponding halogen acids, boiling, and then absorbing the HCNS, which distills over, in a test tube containing  $\text{FeCl}_3$ , when characteristic red  $\text{Fe}(\text{CNS})_3$  will be formed.

#### CYANIDES

1. Cyanides will have been detected by the odor of HCN in the preliminary examination with HCl and concentrated  $\text{H}_2\text{SO}_4$ .
2. To a portion of the prepared solution, add 2 cc. of NaOH solution, and treat with a little  $\text{FeSO}_4$  and a few drops of  $\text{FeCl}_3$ ; heat gently for a short time and then acidify with HCl. A blue precipitate of  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  proves the presence of a cyanide (see reaction 3 under *Cyanides*).

#### NOTES

The presence of a ferricyanide, ferrocyanide, or thiocyanate interferes with test 2. When these are present, proceed as follows: Put into a small distilling flask about 15 cc. of water that has been saturated with  $\text{CO}_2$ , add an excess of solid  $\text{NaHCO}_3$ , and finally some of the powdered original substance. Quickly stopper the flask and distill *under a hood*, catching the distillate in a little NaOH solution, and apply test 2. The HCN contained in the distillate is derived *only* from the simple cyanide by the action of the relatively stronger carbonic acid.

The method of Barnebey may also be employed to advantage. This test depends upon the fact that alkali cyanide solutions have a solvent action on CuS. Render 10 cc.  $\frac{N}{10}$   $\text{CuSO}_4$  alkaline with  $\text{NH}_4\text{OH}$  and treat with a few bubbles of  $\text{H}_2\text{S}$ . Divide the suspension of CuS thus formed into 2 portions; and to one add a little of the prepared solution and shake. Compare the

tubes. A bleaching of the color in the treated tube shows the presence of a cyanide.

### SULPHIDES

1. Most sulphides will have been detected in the preliminary treatment with dilute HCl by the evolution of H<sub>2</sub>S, which may be recognized by its odor and by its property of turning lead acetate paper black.

2. If *aqua regia* or strong HNO<sub>3</sub> is used to get a sulphide into solution, the latter will be oxidized to sulphate with more or less separation of sulphur.

3. If treatment with HCl does not effect the decomposition of a sulphide, add Zn and dilute H<sub>2</sub>SO<sub>4</sub> to the substance contained in a test tube, loosely stoppered with a cork covered with filter paper moistened with lead acetate, and allow the mixture to stand for some time. Sulphides which do not respond to test 1 are usually decomposed by this treatment, yielding H<sub>2</sub>S, which will blacken the lead acetate paper.

4. Sulphides unattacked by acids should be fused with a little NaOH on a porcelain crucible cover; if the melt is placed on a bright silver coin and moistened with a drop of water, a black stain due to Ag<sub>2</sub>S will form.

It must be remembered, however, that sulphates in the presence of organic matter may be reduced to sulphides when fused with NaOH, and thus give the final test.

### GROUP III

#### Brown Ring Test

### NITRATES

1. Acidify a portion of the prepared solution or the concentrated water extract of the original substance with dilute H<sub>2</sub>SO<sub>4</sub>, then add an equal volume of concentrated H<sub>2</sub>SO<sub>4</sub>, and cool thoroughly in a stream of running water. Incline the tube and carefully add 2 to 3 cc. of a strong freshly prepared FeSO<sub>4</sub> solution, and allow the mixture to stand. In the presence of a nitrate, a brown coloration will form at the junction of the two liquids.

## NOTES

Chromates, iodides, bromides, chlorates, ferricyanides, ferrocyanides, and permanganates interfere with the test. Nitrites give the same reaction (see reaction 2). Iodides and bromides in contact with concentrated  $H_2SO_4$  are partially oxidized with the liberation of free I and Br; these, by coloring the solution, interfere with the test. The halides may be removed by precipitation with  $Ag_2SO_4$  (free from nitrates). Chromates will be reduced by  $FeSO_4$ , yielding green  $Cr_2(SO_4)_3$ , which will obscure the brown color. Permanganates by their strong purple color will mask the reaction. Both chromates and permanganates may be removed by adding solid  $Na_2SO_3$  and dilute  $H_2SO_4$ , boiling until the solution is green, and then precipitating the Cr and Mn salts with an excess of  $Na_2CO_3$ . Filter, acidify the filtrate with dilute  $H_2SO_4$ , and make the test on the resulting solution. Chlorates interfere on account of  $ClO_2$ , which will form on adding concentrated  $H_2SO_4$ ; these will also be reduced by the above treatment. Ferro- and ferri-cyanides yield with  $FeSO_4$  blue precipitates, and hence interfere with the reaction. These may be removed by the addition of ferrous and ferric salts and a little dilute  $H_2SO_4$ , heating the mixture to boiling, and adding  $BaCl_2$  to precipitate the  $H_2SO_4$ . The  $H_2SO_4$  and  $BaCl_2$  are added to form heavy  $BaSO_4$ , which will have the effect of carrying down the blue precipitates, which are difficult to filter when alone. Although provision is made for the removal of interfering elements, these are of rare occurrence in mixtures ordinarily met with. The coloration test is therefore the one most frequently employed for the detection of the nitrates.

2. **Reduction to Ammonia.** Render either the aqueous extract of the original substance or the prepared solution strongly alkaline with  $NaOH$ , and boil with stirring until no more ammonia is given off. Add some aluminum turnings, or a mixture of granulated zinc and iron filings, and heat again. In the presence of a nitrate or nitrite, the odor of ammonia will be evident (see reaction 5 under *Nitrates*).

## NITRITES

1. Nitrites will have been detected in the preliminary examination with dilute  $HCl$ ; the  $NO_2$  fumes given off may be readily detected by their property of turning starch-iodide paper blue.

2. **Brown Coloration Test.** The same as with nitrates except that in this case acetic acid or dilute  $H_2SO_4$  may be used instead of concentrated  $H_2SO_4$ .

## ACETATES

1. Acetates are detected in the preliminary treatment of the original substance with concentrated  $H_2SO_4$  by the odor of vinegar.
2. Treat some of the original solid substance contained in a small evaporating dish or beaker with 1 to 2 cc. of amyl alcohol and 5 cc. of concentrated  $H_2SO_4$ , and heat *gently*. The characteristic odor of amyl acetate ("pear essence") indicates the presence of an acetate. If ethyl alcohol is used, the odor of ethyl acetate will be made evident on warming the mixture (see reaction 2 under *Acetates*).

## CHLORATES

1. Chlorates are recognized by their behavior when treated with concentrated  $H_2SO_4$ . Heat about 1 cc. of concentrated  $H_2SO_4$  in a test tube, remove from the flame, and under a hood (*pointing mouth of tube toward back of hood*) add a very *minute* amount of the original substance. In the presence of a chlorate, greenish yellow  $ClO_2$  will be evolved; the evolution is accompanied by a slight explosion if the gas is sufficiently heated.
2. In the *absence* of halogen acids, a small portion of the solid substance is ignited in a small porcelain dish at a temperature just below a red heat; it is then cooled, extracted with water, transferred to a test tube, and finally treated with a few drops of silver nitrate. A white curdy precipitate of  $AgCl$  proves the presence of a chlorate.
3. If halogen acids are *present*, they must be removed by adding to the boiling solution acidified with  $HNO_3$  an *excess* of  $AgNO_3$  and filtering. To the filtrate, the volume of which should be 50 cc., add 5 cc. conc.  $HNO_3$  and 5 cc. saturated  $SO_2$  solution. Heat. A white precipitate of  $AgCl$  proves the presence of a chlorate. (See reaction 4 under *Chlorates*.)



## PART III

### ANALYSIS OF GROUP III. (METALS) IN THE PRESENCE OF ORGANIC MATTER, PHOSPHATES, OXALATES, ETC.

THE phosphates, fluorides, oxalates, borates, and silicates of the metals of Groups III. and IV., including Mg, are soluble in mineral acids, but are precipitated when the free acid which holds them in solution is neutralized by ammonium hydroxide. Should any of these acids be present in the original solution, they will offer no difficulties in the analysis of Groups I. and II., for in these the solution is kept acid. On proceeding, however, to precipitate Group III. the solution is first rendered alkaline, and, as a consequence, there will be precipitated along with the metals of Group III. part or all of the metals of Group IV. as phosphates, oxalates, etc., depending upon the quantity of these acid radicals present. It is evident, therefore, that a different procedure from that given must be followed for the analysis of Group III. if these acids are present.

It will be recalled that certain non-volatile organic acids and compounds, as tartaric acid, citric acid, sugar, and starch, hinder the precipitation of the trivalent elements Al, Cr, and Fe(-ic) as hydroxides and basic acetates. For this reason, before proceeding with the Third Group analysis, it is necessary to test for non-volatile organic matter, and, if found, to remove it. The presence of organic matter will have been indicated on heating a small portion of the original substance in a tube closed at one end. Blackening of the residue, accompanied by a burnt odor, indicates the presence of organic matter. If the substance under examination is a solution, evaporate a small portion to

dryness, heat to a dull red heat, and look for indications of organic matter.

**Test for an Oxalate.** To a small portion of the filtrate from Group II., from which the  $H_2S$  has been expelled, add an excess of  $Na_2CO_3$ , boil vigorously for a moment, and filter. Render the filtrate slightly acid with acetic acid, boil off the  $CO_2$ , and then add an equal volume of a saturated  $CaSO_4$  solution; a white crystalline precipitate proves the presence of an oxalate.

*Organic matter and oxalates may both be removed* by the following procedure: To the residue obtained by evaporating the filtrate from Group II. to dryness, add 5 cc. conc.  $H_2SO_4$  and heat gently until the mass has completely charred. Cool. Add 5 cc. conc.  $HNO_3$  and heat (gently at first) until fumes of  $SO_3$  are given off. Cool. Add 5 cc. more conc.  $HNO_3$  and evaporate again to  $SO_3$  fumes. Repeat this treatment with  $HNO_3$  and evaporating to  $SO_3$  fumes until the solution is either colorless or possesses only a faint straw color. (Three treatments are generally sufficient.) Cool. Cautiously dilute with 25 cc. water, boil to expel gases and filter using a double filter. Analyze the filtrate for Groups III. and V. and for Ca, if the latter is not found in the residue. The residue may consist of  $BaSO_4$ ,  $SrSO_4$ ,  $CaSO_4$  and anhydrous  $Cr_2(SO_4)_3$ . Boil the residue for 10 minutes with 20 cc. of a saturated  $Na_2CO_3$  solution and filter. Wash the residue until the washings after being acidified with  $HCl$ , fail to give a test for sulphates. Reject filtrate and washings. Heat residue with 15 cc. dil.  $HNO_3$  and filter. Analyze filtrate for Cr, Ba, Sr, and Ca.

**Test for Phosphates.** To about 2 cc. of the filtrate from Group II., from which the  $H_2S$  has been removed, add a few drops of concentrated  $HNO_3$  and evaporate nearly to dryness; take up with a little dilute  $HNO_3$ , transfer to a test tube, add an equal volume of ammonium molybdate solution, and heat gently (*do not boil*). A yellow precipitate of  $(NH_4)_8PO_4 \cdot 12 MoO_3$  proves the presence of a phosphate.

**Silicates**, if present, should have been detected in the preliminary examination of the solid substance with a  $NaPO_3$  bead; and should have been removed, preferably before proceeding with

the metallic analysis, by evaporating the solution acid with HCl or HNO<sub>3</sub>\* to dryness, desiccating at 120°, extracting the residue with a few cc. of concentrated HCl,\* diluting, heating, and filtering off the dehydrated and insoluble silica. The latter may then be verified by the NaPO<sub>3</sub> bead test, or by treatment in a platinum crucible with CaF<sub>2</sub> and concentrated H<sub>2</sub>SO<sub>4</sub>, heating, and testing the escaping vapor with a drop of water (see reaction 1, page 132).

If, however, the analysis has been begun without regard to the presence of silicates, the filtrate from Group II. should be tested for this acid radical, and, if found, removed by the procedure just outlined, before proceeding to precipitate Group III.

Borates and fluorides are usually held in solution by the NH<sub>4</sub>Cl present, and hence in their presence no modification of the usual scheme need be made.

#### Outline of Method to be Used in the Presence of Phosphates

Oxalates, silicates, fluorides, borates, and non-volatile organic matter having been disposed of, it only remains to provide a method of analysis for the Third Group metals which shall include the presence of phosphates. The scheme which follows is based upon the fact that of the phosphates of Groups III. and IV., only those of Al, Cr, and Fe(-ic) are insoluble in acetic acid; if, therefore, the iron is oxidized and the free HCl is replaced by acetic acid, part or all of the trivalent metals present will be precipitated as phosphates, depending upon the quantity of phosphoric acid present. If the amount of PO<sub>4</sub> is less than that required to combine with all of the Fe(-ic), Al, and Cr, the precipitate which forms will contain all the PO<sub>4</sub>. If, on the other hand, the quantity of PO<sub>4</sub> present exceeds that required to unite with the trivalent metals, it will be evident that more trivalent metals will have to be added to completely precipitate the PO<sub>4</sub>. The metallic radical used for this purpose is Fe(-ic), partly because its phosphate is the least soluble in acetic acid, but chiefly because it is possible, when a salt of ferric iron is used, to tell when all the phosphate has been precipitated; for

\* If metals of the first group are present, use HNO<sub>3</sub> instead of HCl.

when this condition is reached, any excess of ferric salt added will yield with the acetate radical present red ferric acetate, which can readily be recognized by its color. Now, on adding an excess of  $\text{NaC}_2\text{H}_3\text{O}_2$ , largely diluting, boiling the solution, and rapidly filtering, the separation of all of the trivalent metals, including the excess of iron added, together with all the phosphoric acid, is accomplished (see reactions 6 and 7 under *Iron*, pages 83 and 84). The filtrate, now free from  $\text{PO}_4$ , is concentrated by evaporation, and then treated for the remaining metals of Groups III. and IV. in the usual way.

### The Phosphate Separation

If phosphates are shown to be present, the entire filtrate from Group II. is boiled until all of the  $\text{H}_2\text{S}$  is expelled, a few drops of concentrated  $\text{HNO}_3$  are then added, and the solution boiled for several minutes to insure the complete oxidation of the iron present. Test a separate small portion, about 2 cc., for iron by adding a few drops of  $\text{K}_4\text{Fe}(\text{CN})_6$ . A blue precipitate proves the presence of iron. The remainder of the solution is transferred to a beaker of 500 cc. capacity and is treated with ammonium hydroxide, added drop by drop with vigorous stirring, until a slight precipitate is produced which persists after stirring for 3 minutes. Now add *cautiously*, with constant stirring, dilute  $\text{HCl}$ , drop by drop, until a clear solution is obtained; then add 8 g. of  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  and 8 cc. of 50 per cent. acetic acid. If the solution is not red, add  $\text{FeCl}_3$  solution drop by drop, with stirring, until the solution assumes a deep red color, avoiding an excess. In the presence of a precipitate, the color of the solution may be seen by filtering a small portion; the filtrate should give, when made alkaline with  $\text{NH}_4\text{OH}$ , a reddish brown precipitate of  $\text{Fe}(\text{OH})_3$ , showing that an excess of  $\text{Fe}(\text{-ic})$  is present; if a light-colored precipitate is obtained with  $\text{NH}_4\text{OH}$ , more  $\text{FeCl}_3$  should be added. Now dilute the solution with *hot* water to 400 cc., heat *rapidly* to boiling, and boil for 3 minutes only. Allow the precipitate to settle, filter on a large fluted filter contained in a 10 cm. funnel, and wash

with hot water. The residue may consist of the phosphates and basic acetates of Al, Cr, and Fe (-ic), and it may also contain small amounts of Ni, Mn, and Zn. The filtrate, which should not have a yellow color, is at once evaporated in a large evaporating dish to 50 cc., and any precipitate which separates out is filtered off and rejected. The filtrate, now concentrated and free from  $\text{PO}_4$ , is analyzed as usual for Groups III., IV., and V.; the tests for Al, Cr, and Fe should be omitted, as these metals will be in the residue from the basic acetate separation. The precipitate, consisting of the phosphates and basic acetates of Al, Cr, and Fe (-ic), is transferred to a beaker with the aid of 20 cc. of water, 2 g.  $\text{Na}_2\text{O}_2$  are added, the mixture is boiled, with stirring, and finally filtered. The residue, consisting of  $\text{Fe(OH)}_3$ , is rejected. The filtrate may contain  $\text{Na}_3\text{AlO}_3$ ,  $\text{Na}_2\text{CrO}_4$ ,  $\text{Na}_3\text{PO}_4$ , and an excess of NaOH. If the solution is yellow, chromium is present; if colorless, Cr is absent. Aluminum is detected by acidifying the solution with  $\text{HNO}_3$  and then rendering alkaline with ammonium hydroxide; the white gelatinous precipitate of  $\text{AlPO}_4$  or  $\text{Al}(\text{OH})_3$  is filtered off, washed with hot water several times, and the presence of aluminum is confirmed by igniting with a few drops of  $\text{Co(NO}_3)_2$  in the usual way. The filtrate will contain the chromium as  $\text{Na}_2\text{CrO}_4$ .

## PREPARATION OF THE SOLUTION

The preliminary tests completed, the next step in the systematic examination is to get the substance into solution. This is accomplished by the use of the solvents, water, nitric acid, hydrochloric acid, and *aqua regia*. In determining the solvent, it is advisable to experiment with small portions of the original substance at first, finally treating, after the proper solvent has been found, about one gram of the original material for the analysis. With mixtures, more than one solvent may be required. In such a case, it is a good plan to keep, and analyze separately, portions dissolved by different solvents; the additional labor involved will be compensated by the information

which this procedure will supply concerning the manner in which the metallic and acid radicals are united.

### *Treatment with Water*

Treat a small quantity of the finely powdered substance with about 25 cc. of water and heat to boiling. If solution takes place, treat one gram of the sample in the same way and analyze the resulting solution for the metals and acids. Test the aqueous solution with litmus; if alkaline, the presence of a carbonate, hydroxide, sulphide, phosphate, borate, or cyanide is indicated; if acid, it may point to an acid salt, free acid, or the salt of a heavy metal. If no solution appears to have taken place, filter, and evaporate some of the clear filtrate on a watch glass to dryness; if only a slight residue remains, the substance may be considered insoluble in water; if a moderate amount of residue is left, it indicates that the mixture contains a water-soluble component. In that case, treat a gram sample with boiling water and filter. Analyze the aqueous extracts for acids and bases. Treat the residue with acids as given below.

### **NOTES**

If iodides or bromides, particularly the former, have been indicated in the preliminary test with conc.  $H_2SO_4$ , the original substance, whether it dissolves wholly or in part in water, must be treated for the removal of these halides before the analysis for the metals is begun. This is accomplished by treating the substance with  $HNO_3$  and heating until no more I is evolved. If iodides are not removed, there will be danger of forming *explosive* brownish black nitrogen iodide, in making the preliminary test for Group III., because of the action of iodine set free by the treatment with  $HNO_3$  on the ammonia which is next added.

### *Treatment with Acids*

If the substance is insoluble in water, treat it or the residue from the water treatment successively with hot dilute HCl and hot concentrated HCl. If these fail to effect solution, try the action of dilute and concentrated  $HNO_3$  on separate small portions; if these also fail, add HCl to the mixture containing  $HNO_3$ , thus forming *aqua regia*, and heat. If still insoluble,

examine it by the method given for "*Insoluble Substances*," page 197.

#### NOTES

1. During the treatment with HCl, indications of the presence of certain acids will be given (see "*Preliminary Examination*," page 162).
2. If Hg and As are present, boiling with HCl may cause these elements to be lost by volatilization; the remedy is to be sought in the use of HNO<sub>3</sub>, which oxidizes them into compounds which are not readily volatile.
3. If complete solution with HCl is obtained, the absence of Ag, Hg (-ous), and large amounts of Pb is indicated. Evaporate the solution nearly to dryness to expel most of the acid, dilute, and analyze the resulting solution, beginning with Scheme II.
4. Treatment with concentrated HCl may cause the precipitation of Pb in the form of crystalline needles of PbCl<sub>2</sub>; when this is the case, filter them off, dissolve in boiling water, and test for Pb.
5. If the HCl treatment causes gelatinous silicic acid to separate, evaporate the mixture on the water bath to dryness, dehydrate by heating to 120° C. for half an hour, extract with 3 cc. of hot concentrated HNO<sub>3</sub> or HCl, dilute, heat, and filter off the SiO<sub>2</sub>. The filtrate is then examined for the metals.
6. If HNO<sub>3</sub> has been used as a solvent, boil the liquid down to about 1 cc., dilute with 20 cc. of water, and if the solution clouds on dilution, clear with a few drops of HNO<sub>3</sub> and analyze the solution for all groups.
7. When *aqua regia* is employed, the smallest possible amount should be used; the solution should then be evaporated down to about 1 cc. to destroy the excess, diluted with 15 cc. of water, and the chlorides of Group I. filtered off and analyzed. The filtrate is treated with 5 cc. of concentrated HCl and again evaporated down to 1 cc., diluted somewhat, and analyzed for the metals, beginning with Group II.
8. With few exceptions, the following substances, while insoluble in water, are dissolved by boiling HCl or HNO<sub>3</sub>: all phosphates, arsenates, arsenites, borates, carbonates, oxalates, and tartrates (the alkali salts are soluble in water); also the oxides, hydroxides, sulphides of the heavy metals, alumina, magnesia, and a number of metallic iodides and cyanides. Oxides of Al, Fe, and Cr which have heated intensely do not dissolve readily in these acids.
9. Because of its oxidizing action, HNO<sub>3</sub> dissolves sulphides and most metals and alloys which are not attacked by HCl; the latter, on the other hand, dissolves the oxides of Sn and Sb, as well as MnO<sub>2</sub>, all of which are not dissolved by HNO<sub>3</sub>.

## METALS AND ALLOYS

From 0.5 to 1 gram of the metal or alloy, in the form of shavings, foil, filings, or turnings, is treated with 20 cc. of  $\text{HNO}_3$  sp. gr. 1.2) and is heated gently (under a hood) until no more red fumes of  $\text{NO}_2$  are given off; it is then diluted with an equal volume of water, heated again for a few minutes, and filtered if necessary. If complete solution takes place, the absence of Au, Pt, Sb, and Sn is shown; \* in that case, expel the excess of  $\text{HNO}_3$  by evaporation, dilute with water, and analyze the solution for all groups except IV. and V. Mg, however, must be included.

(a) If a metallic residue is left, it is probably Pt or Au †, or both.

(b) If a white residue is left which is insoluble on dilution and heating, it may consist of hydrated  $\text{SnO}_2$  or  $\text{Sb}_2\text{O}_5$ , or both, admixed with arsenic in the form of tin arsenate, phosphorus in the form of tin phosphate, bismuth as  $\text{Bi}_2\text{O}_3$ , and traces of Cu and Pb. Filter.

<p><b>Filtrate.</b> Evaporate to drive off excess of <math>\text{HNO}_3</math>. Add HCl to ppt. 1st group and filter. Analyze residue for Group I. Treat filtrate with <math>\text{H}_2\text{S}</math> and filter. Analyze filtrate for Group III. and Mg. Dissolve residue in hot dil. <math>\text{HNO}_3</math> and unite with solution of residue 2.</p>	<p>Dry and fuse residue in a porcelain crucible with 4 times its weight of a mixture of equal parts of <math>\text{Na}_2\text{CO}_3</math> and S; cool, extract melt with hot water, and filter.</p>	<p>Residue 2 is <math>\text{CuS}</math>, <math>\text{Bi}_2\text{S}_3</math>, <math>\text{PbS}</math>. Dissolve in hot dil. <math>\text{HNO}_3</math> and combine with the corresponding solution obtained from the first filtrate and proceed as directed in the analysis of the main filtrate in Scheme II. A.</p>	<p>Filtrate will contain the As, Sb, and Sn as thio-salts + an excess of <math>\text{Na}_2\text{S}</math>. Just acidify with HCl, filter, and reject filtrate. Residue may consist of <math>\text{As}_2\text{S}_3</math>, <math>\text{Sb}_2\text{S}_5</math>, and <math>\text{SnS}_2 + \text{S}</math>; analyze according to Scheme II. B.</p>
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\* Minute amounts of Sb dissolve completely in  $\text{HNO}_3$ ; silver alloys containing a very small amount of Pt are completely dissolved by  $\text{HNO}_3$ .

† A black residue of carbon or graphite is sometimes left.

## NOTES

1. If solution of the alloy does not readily take place, and Pt and Au are absent, treat with HCl; the latter is more satisfactory than HNO<sub>3</sub> as a solvent for Al, since the latter is only difficultly soluble in HNO<sub>3</sub>. HNO<sub>3</sub> is used instead of HCl, first, because it is the better solvent for metals and alloys; second, because treatment with HCl would convert any P, S, and As usually present as phosphide, sulphide, and arsenide, respectively, into PH<sub>3</sub>, H<sub>2</sub>S and AsH<sub>3</sub>, which would be lost by volatilization. HNO<sub>3</sub> oxidizes these elements to their corresponding acids, viz.: H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>AsO<sub>4</sub>. Only these acids together with H<sub>2</sub>SiO<sub>3</sub> need to be tested for in the analysis of alloys.

2. A small white residue may be boiled with concentrated HCl and the resulting liquid divided into two portions. One portion is tested with Pt and Zn couple for Sb. The other is heated with an iron nail for some time and the clear decanted solution tested for Sn by the addition of HgCl<sub>2</sub>.

3. A portion of the HNO<sub>3</sub> filtrate may be tested for H<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>, and, if found, P and S reported.

## INSOLUBLE SUBSTANCES

By an insoluble substance we mean one which cannot be got into solution by the action of the acids taken singly or together.

The most common insoluble substances are the following:—

C, S, Ag<sub>3</sub>Fe(CN)<sub>6</sub>, Ag<sub>4</sub>Fe(CN)<sub>6</sub>, AgCN, AgCl, AgBr, AgI, BaSO<sub>4</sub>, SrSO<sub>4</sub>, CaSO<sub>4</sub>, PbSO<sub>4</sub>, PbCl<sub>2</sub>, fused PbCrO<sub>4</sub>, ignited or anhydrous chromic salts, ignited and native oxides, as Al<sub>2</sub>O<sub>3</sub> (corundum), Fe<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub> (cassiterite), Cr<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> · FeO (chrome-iron ore), CaF<sub>2</sub>, Sb<sub>2</sub>O<sub>4</sub>, Fe<sub>4</sub>[Fe(CN)<sub>6</sub>]<sub>3</sub>, SiO<sub>2</sub>, and certain silicates.

Carbon is generally recognized by its black color, insolubility in *aqua regia*, and combustibility when heated strongly on platinum foil. When heated with KNO<sub>3</sub>, deflagration ensues with the formation of K<sub>2</sub>CO<sub>3</sub>; this method is not applicable to graphite, the presence of which may be determined by its physical properties.

Sulphur is recognized (in the preliminary testing) by the formation of a yellow sublimate and evolution of SO<sub>2</sub> when heated in a glass tube.

When S and C are present, it is desirable to remove them by roasting in an open porcelain crucible.

Treatment with *aqua regia* will have converted the simple and complex cyanides, as well as all the halides of Ag, into  $\text{AgCl}$ ; the latter dissolves to a large extent in the strong acids, but separates out again when the latter are diluted. Long treatment with *aqua regia* will dissolve prussian blue, but the following method is preferable for complex insoluble cyanides in general: Boil the substance with a strong solution of  $\text{NaOH}$ , dilute and filter; the residue will contain the heavy metal as hydroxide, while the filtrate will contain the acid radical in the form of the Na salt and may be examined by the methods already given.\*

$\text{PbSO}_4$  and  $\text{PbCl}_2$  may be dissolved by treatment with hot, strong  $\text{NH}_4\text{C}_2\text{H}_8\text{O}_2$  solution. The extract is divided into three portions: in the first, test for Pb by the addition of a little  $\text{H}_2\text{SO}_4$  or  $\text{K}_2\text{CrO}_4$ ; in the second, test for Cl by diluting, acidifying with  $\text{HNO}_3$ , and adding  $\text{AgNO}_3$ ; and in the third, test for  $\text{SO}_4$  by acidifying with  $\text{HCl}$ , filtering if necessary, and adding  $\text{BaCl}_2$ .

Sulphates of the Alkaline Earth Metals are best fused in a platinum crucible with five times their weight of anhydrous  $\text{Na}_2\text{CO}_3$ ; the melt is then completely extracted with hot water, filtered, and the residue is *thoroughly* washed with water. The residue will consist of the carbonates of alkaline earths, which may readily be got into solution with hydrochloric acid, and the resulting solution tested in the usual way. The water extract will contain the acid radical as  $\text{Na}_2\text{SO}_4$  and an excess of  $\text{Na}_2\text{CO}_3$ .

$\text{SrSO}_4$ ,  $\text{CaSO}_4$ , and  $\text{PbSO}_4$  may be quantitatively converted into the corresponding carbonates by prolonged boiling with a concentrated  $\text{Na}_2\text{CO}_3$  solution. If the residue after filtering is *thoroughly* washed free from alkali, it may then readily be dissolved by acid.

$\text{BaSO}_4$  requires several treatments for its complete transformation by  $\text{Na}_2\text{CO}_3$  solution. One treatment changes about 80 per cent. of this sulphate into carbonate.

\* For method of analysis of insoluble double cyanides not precipitated by excess of  $\text{NaOH}$ , see page 151 under *Ferrocyanides*, reaction 3.

**Fused  $PbCrO_4$ ,  $Cr_2O_3$ , Chrome Iron Ore and Ignited Chromic Salts** are best fused with  $Na_2O_2$  in a nickel crucible or with a mixture of  $Na_2CO_3$  and  $NaNO_3$ . By this treatment, soluble  $Na_2CrO_4$  is formed, which after treatment with water is separated by filtering and tested for in the filtrate.

**$SnO_2$  and  $Sb_2O_3$**  are got into solution by fusing in a porcelain crucible with three times their weight of  $Na_2CO_3$  mixed with an equal quantity of S. The melt is extracted with hot water and filtered. The filtrate will contain the Sb and Sn in the form of thio-salts ; it is just acidified and the precipitate treated according to Scheme II. B.

**$Al_2O_3$  and  $Fe_2O_3$**  are fused in platinum with  $KHSO_4$  or  $K_2S_2O_7$ , whereby they are converted into soluble sulphates. Fusion with  $Na_2CO_3$ , followed by acid treatment, also takes these oxides in solution.

**Silver Halides** may be treated by one of the following two methods :—

1. Fuse with  $Na_2CO_3$  in a porcelain crucible. The product will consist of metallic silver and the sodium salts of the halides ; extract with water and filter. Test the residue for Ag and the filtrate for halogens.

2. Treat with Zn and dilute  $H_2SO_4$  in a crucible or small dish ; allow the action to continue for 20 minutes, and then filter. Test the residue for Ag and the filtrate for halogens.

**$SiO_2$  and Silicates** are recognized by the "skeleton"  $NaPO_3$  bead.

Silicates are usually decomposed by fusing with five times their weight of a mixture of equal parts of anhydrous  $Na_2CO_3$  and  $K_2CO_3$ , to which about 0.1 g. of  $KNO_3$  is added. This will be taken up more fully in the systematic treatment.

**$CaF_2$**  is decomposed by heating the finely ground material with concentrated  $H_2SO_4$  in a platinum dish or crucible, and evaporating until no more  $SO_3$  fumes are given off. The residue will be  $CaSO_4$  ; extract it with water for some time and filter. Test the filtrate for Ca with  $(NH_4)_2C_2O_4$ .

### Systematic Treatment of Insoluble Substances

Before proceeding with the systematic treatment of a residue insoluble in acids, it is desirable to make the following preliminary tests :—

1. Examine the residue carefully with a lens and determine whether or not the substance is homogeneous.
2. Determine whether free C and S are present : if present, remove by roasting.
3. Chromic oxide is green and will be made evident by yielding a green bead with  $\text{NaPO}_3$  which is unaffected by the reducing flame ; at the same time, indications of  $\text{SiO}_2$  or of a silicate will also be obtained.
4. If the substance is *white*, treat it with a little  $(\text{NH}_4)_2\text{S}$ . If it blackens, the presence of Ag or Pb salts is indicated ; confirm as directed in (5).
5. If *black or colored*, mix a small amount with  $\text{Na}_2\text{CO}_3$  and heat on charcoal with a reducing flame ; a lustrous malleable globule shows the presence of either Pb, Ag, or Sn. Flatten the globule in a mortar and heat with dilute  $\text{HNO}_3$ . A clear solution indicates the absence of Sn ; a white residue, the presence of Sn. Divide the  $\text{HNO}_3$  solution into two portions. To the first add HCl ; a white precipitate soluble in  $\text{NH}_4\text{OH}$  shows the presence of Ag. To the second portion add dilute  $\text{H}_2\text{SO}_4$  ; a white precipitate is  $\text{PbSO}_4$ . If no globule is obtained and the white substance is not blackened by  $(\text{NH}_4)_2\text{S}$ , the absence of Pb and Ag is shown.
6. Flame Test. Take up some of the material on a moistened Pt wire and hold in the reducing flame for some time. The reducing flame will change the sulphates of the alkaline earths to sulphides. Moisten the wire with a drop of HCl and hold in the colorless bunsen flame. Alkaline earths impart their characteristic colorations to the flame.
7. If test 3 above is found unsatisfactory for  $\text{SiO}_2$  and Cr, the following may be used :—

$\text{SiO}_2$ . Mix the finely powdered substance in a platinum crucible or lead tube with a small quantity of  $\text{CaF}_2$  ( $\text{SiO}_2$  free), add

concentrated  $H_2SO_4$ , and warm. Hold in the escaping vapors a drop of water on the loop of a Pt wire; if the drop becomes turbid,  $SiO_2$  is present.

**Chromium.** Prepare a  $Na_2CO_3$  bead. Take up a little of the substance mixed with  $KClO_3$  and heat. Place bead in about 1 cc. of water and heat. A yellow solution indicates Cr.

#### Scheme for the Treatment of Insoluble Substances

If the substance contains Pb salts, these may readily be removed by repeatedly digesting with hot  $(NH_4)_2C_4H_4O_6$  or  $NH_4C_2H_3O_2$  solution, filtering, and testing the filtrate for Pb,  $SO_4$ , and Cl. The residue, which should be thoroughly washed and tested until free from Pb salts [shown by wash water no longer reacting with  $(NH_4)_2S$ ], is then treated with KCN solution to dissolve AgCl, AgBr, AgI, and AgCN, filtered, and washed. The treatment with KCN is given only when Ag salts are shown to be present by preliminary test with Zn +  $H_2SO_4$ . The KCN extract is tested for Ag by adding  $(NH_4)_2S$ , filtering off the  $Ag_2S$ , washing, and dissolving in hot dilute  $HNO_3$ . To the clear solution, add HCl; a white precipitate is AgCl. If S and C are present, heat in an open porcelain crucible till all C and S are oxidized. Mix the substance, now free from Pb and Ag salts, in a platinum crucible with six times its weight of a mixture of equal parts of anhydrous powdered  $K_2CO_3$  and  $Na_2CO_3$  + 0.1 g. of  $KNO_3$ . (If reducible metals have not been removed, treat in a Ni crucible. Porcelain cannot be used, as it gives up  $SiO_2$ , Ca, and Al to the melt.) Heat over a blast lamp till the mass is in a state of quiet fusion. Remove flame. When cool, transfer crucible to a casserole or evaporating dish, and extract with boiling water. Break up the mass with pestle during extraction. Allow finally to settle, and filter.

Filtrate may contain  $\text{Na}_2\text{SiO}_3$ ,  $\text{Na}_2\text{CrO}_4$ ,  $\text{NaF}$ ,  $\text{Na}_3\text{PO}_4$ ,  $\text{Na}_3\text{AlO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{SnO}_3$ ,  $\text{Na}_3\text{AsO}_4$ , ( $\text{NaSbO}_3$ ),  $\text{Na}_2\text{MnO}_4$ ,  $\text{Na}_3\text{BO}_3$  and  $\text{Na}_2\text{CO}_3$ , as well as K salts of these acids. Divide into two equal portions.

*1st portion.* Acidify with HCl and add a small portion to the  $\text{HNO}_3$  solution of the residue; if no ppt. forms, unite the two filtrates, evap. to dryness, dehydrate  $\text{SiO}_2$  by heating at  $120^\circ \text{C}$ . till all HCl is driven off. Extract the residue with 25 cc. of conc. HCl, stir thoroughly, add 25 cc. of water, and boil with stirring; filter.

<b>Residue:</b> $\text{SiO}_2$	Heat filtrate to boiling and treat with $\text{H}_2\text{S}$ . Without filtering, dilute with cold water to 100 cc. and saturate again with $\text{H}_2\text{S}$ . Filter. Analyze residue for II. A and II. B. Analyze filtrate for all other groups.
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*2d portion.* Treat for acids.

Residue may consist of  $\text{BaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ , possibly  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{SnO}_2$ , and unattacked  $\text{SiO}_2$ , and in some cases nearly any metal or its oxide; wash several times with hot water. Treat with hot dil.  $\text{HNO}_3$  and filter.

<b>Filtrate</b> is to be united with HCl solution of aqueous extract of melt unless a ppt. forms; in that case, keep the solutions separate. The ppts. produced by the same group reagents may be united and examined together.	Residue may consist of $\text{SiO}_2$ , $\text{SnO}_2$ , and $\text{Al}_2\text{O}_3$ . Fuse in a Ni crucible with $\text{NaOH}$ . Extract with water and filter. Filtrate contains $\text{Na}_2\text{SnO}_3$ , $\text{Na}_3\text{AlO}_4$ + $\text{Na}_3\text{SiO}_4$ . Test for Al and Sn, if not already found.
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#### DETECTION OF ALKALIES IN INSOLUBLE SILICATES

**The J. Lawrence Smith Method.** One gram of the finely ground mineral is first pulverized in an agate mortar with its own weight of C.P.  $\text{NH}_4\text{Cl}$ , and the resulting mixture is then thoroughly mixed with 8 grams of alkali-free  $\text{CaCO}_3$  and heated in a covered platinum crucible, gently at first and finally to a dull red heat, for 40 minutes. The crucible should be placed in a hole made in a piece of thick asbestos board in such a way that only two-thirds of the crucible can be directly heated by the burner. The mass does not fuse but sinters. The active agent is fused  $\text{CaCl}_2$ , which decomposes the silicate with the formation of chlorides of the alkali metals. After cooling, the crucible with its contents is transferred to a casserole, boiled with water, and the  $\text{CaO}$  is allowed to slake. The last opera-

tion may be hastened by crushing any lumps with a pestle. After standing for one hour, the mixture is filtered, and the filtrate is freed of lime by rendering it alkaline with ammonium hydroxide, heating, adding  $(\text{NH}_4)_2\text{CO}_3$  to complete precipitation, and finally a little  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . Filter, evaporate the filtrate to dryness, and ignite the residue to drive off  $\text{NH}_4$  salts. The residue is then treated in the usual way for K and Na.

### Acid Analysis of Minerals and Metallurgical Products

With a few exceptions, minerals and slags need only be tested for sulphides, carbonates, silicates, phosphates, borates, sulphates, fluorides, and chlorides. Carbonates and sulphides may be detected by treatment with HCl, and silica or silicates by the  $\text{NaPO}_3$  bead test. In the  $\text{HNO}_3$  solution of the finely powdered substance, the tests for phosphates, chlorides, and sulphates (in the absence of sulphides) may be made. If the chloride is present in an insoluble form, as  $\text{AgCl}$ , it should be treated by one of the methods already mentioned (see page 195). In the absence of sulphides, the test for sulphates may also be made by fusing the original substance with  $\text{Na}_2\text{CO}_3$ , extracting the melt with boiling water, and filtering; the filtrate, after acidifying with HCl and boiling to drive out the  $\text{CO}_2$ , is then treated with  $\text{BaCl}_2$ . If sulphides are present, boil the finely powdered substance, with constant stirring, with a saturated solution of  $\text{Na}_2\text{CO}_3$ , then filter, acidify the filtrate with HCl, and add  $\text{BaCl}_2$ ; or if the original substance dissolves completely in HCl, the resulting solution may be treated with  $\text{BaCl}_2$ . For the detection of fluorides in the presence of silicates, see test 3 under *Fluorides*, page 173. For the detection of borates in silicates undecomposed by concentrated  $\text{H}_2\text{SO}_4$ , see reaction 6 under *Borates*, page 136.

The tests for borates and fluorides, when these occur together in combination with silicates, may be carried out in one sample by fusing about one gram with  $\text{Na}_2\text{CO}_3$ , extracting the mass with boiling water, and filtering. The filtrate will then contain

$\text{Na}_2\text{SiO}_3$ ,  $\text{NaF}$ ,  $\text{NaBO}_2$  + the excess of  $\text{Na}_2\text{CO}_3$ . A portion of this solution, after slightly acidifying with  $\text{HCl}$ , may be tested for boric acid with turmeric paper. The remainder of the aqueous extract is then tested for a fluoride, as described in test 3 under *Fluorides* (see page 173).

## TABLE OF SOLUBILITIES\*

*Showing the classes to which the compounds of the commonly occurring elements belong in respect to their solubility in water, hydrochloric acid, nitric acid, or aqua regia.*

### *Preliminary Remarks*

For the sake of brevity, the classes to which the compounds belong are expressed by letters. These have the following signification:

W or w, soluble in water.

A or a, insoluble in water, but soluble in hydrochloric acid, nitric acid, or in *aqua regia*.

I or i, insoluble in water, hydrochloric acid, or nitric acid. •

Further, substances standing on the border lines are indicated as follows:

W-A or w-a, difficultly soluble in water, but soluble in hydrochloric acid or nitric acid.

W-I or w-i, difficultly soluble in water, the solubility not being greatly increased by the addition of acids.

A-I or a-i, insoluble in water, difficultly soluble in acids.

If the behavior of a compound to hydrochloric and nitric acids is essentially different, this is stated in the notes.

Capital letters indicate common substances used in the arts and in medicine, while the small letters are used for those less commonly occurring.

The salts are generally considered as normal, but basic and acid salts, as well as double salts, in case they are important in medicine or in the arts, are referred to in the notes.

The small numbers in the table refer to notes on the following pages.

\* Taken from Wells' translation of the 16th German edition of Fresenius' *Qualitative Analysis*.

## SOLUBILITY

	POTASSIUM	SODIUM	AMMONIUM	BARIUM	STRONTIUM	CALCIUM	MAGNESIUM	ALUMINUM	CHROMIUM	ZINC	MANGANESE	NICKEL	COBALT	
Oxide .....	W	W	W	W	w-a	W-A	A	A	A&I	A	a <sub>17</sub>	A	A	
Chromate.....	W <sub>1</sub>	w	w	a	I	w-a	w	W-I	W	W	w	a	a	
Sulphate.....	W <sub>12-15</sub>	W	W <sub>14-20-30</sub>	W <sub>9-15</sub>	w-a	W-I	W	W <sub>12-14</sub>	W&I <sub>15</sub>	W	W	W	W	
Phosphate.....	w	W <sub>9</sub>	W <sub>9-15</sub>	a	a	A <sub>11</sub>	a <sub>13</sub>	a	a	w-a	a	a	a	
Borate.....	W <sub>2</sub>	W <sub>9</sub>	w	a	a	a	w-a	a	a	a	a	a	a	
Oxalate.....	W <sub>8</sub>	W	W	w	a	a	A.	a	w-a	a	w-a	a	a	
Fluoride.....	w	w	W	w	w-2	A-I	a-i	W	w	w	w-a	a	w-a	
Carbonate.....	W <sub>4</sub>	W <sub>10</sub>	W	A	A	A	A	a-i	W&I	W	A	A	A	
Silicate.....	W	W	-	a	a	a	a	a-i	a	a	a	a	a	
Chloride.....	W <sub>27</sub>	W <sub>25</sub>	W <sub>21-26</sub>	W <sub>7</sub>	W	W	W	W	W&I	W <sub>26</sub>	W	W	W	
Bromide.....	W	W	w	w	w	w	w	w	w	w&i	w	w	w	
Iodide.....	W	w	W	W	w	w	w	w	w	w	w	w	w	
Cyanide.....	W	w	w	w-a	w	w	w	w	w	a	A	a	a-i	
Ferrocyanide.....	W	w	w	w-a	w	w	w	w	w	A-I	a	i	i	
Ferricyanide.....	W	w	w	w	w	w	w	w	w	w	i	i	i	
Thiocyanate.....	W	w	W	w	w	w	w	w	w	w	w	w	w	
Sulphide.....	W	W	W	W	W	W	W	W-A <sub>45</sub>	a	a	a-i	A <sub>16</sub>	A <sub>18</sub>	a <sub>19</sub>
Nitrate.....	W	W	W	W	W	W	W	W	w	W	w	w	w	W
Chlorate.....	W	w	W	w	w	w	w	w	w	w	w	w	w	w
Tartrate.....	W <sub>5-6-7-22-40</sub>	W <sub>7</sub>	W <sub>6</sub>	a	a	A	w-2	w	w	w	a	w-a	a	w
Citrate.....	w	w	w	w	a	a	w-a	w	w	w	w-a	a	w	w
Malate.....	w	w	w	w&a	w	w-a <sub>47</sub>	w	w	w	w	w	w	w	w
Succinate.....	w	w	w	w-a	w-a	w-a	w	w-a	w	w-a	w	w	w	w-a
Benzoate.....	w	w	w	w	w	w	w	w	w	w	w	w	w	w
Salicylate.....	w	W	W	w-a	w-a	w-a	w	w	w	w	w	w	w	w
Acetate.....	W	w	W	W	w	w-a	W	w	w	w	w	w	w	w
Formate.....	w	w	w	w	w	w	w	w	w	w	w	w	w	w
Arsenite.....	W	w	w	w	a	a	a	a	a	a	a	a	a	a
Arsenate.....	W	W	W	w	a	a	a	a	a	a	a	a	a	a

## Notes to Table of Solubilities

1. Potassium dichromate, W.
2. Potassium borotartrate, W.
3. Hydrogen potassium oxalate, W.
4. Hydrogen potassium carbonate, W.
5. Hydrogen potassium tartrate, W.
6. Ammonium potassium tartrate, W.
7. Sodium potassium tartrate, W.
8. Ammonium sodium phosphate, W.
9. Acid sodium borate, W.

TABLE

FERROUS	FERRIC	SILVER	LEAD	MERCUROUS	MERCURIC	CUPRIC	BISMUTH	CADMIUM	GOLD	PLATINUM	STANNOUS	STANNIC	ANTIMONOUS	
a	A	a	A <sub>24</sub>	A	A	A	a	a	a	a	a&i	A <sub>43</sub>		Oxide
w	w	a	A-I	w-a	w <sub>27</sub>	w <sub>30</sub>	w	w	w	w	w	w		Chromate
W <sub>29</sub>	W	W-A	A-I	w-a	w-a	w-a	w	w	W	w	w	w	w	Sulphate
w	a	A	a	a	a	a	a	a	a	w	a	a	w-a	Phosphate
a	a	a	a	a	a	a	a	a	a	w	a	a	w	Borate
a	a	a	a	a	a	a	a	a	w-a	w	w	w	w	Oxalate
w-a	w	w	a	a	w-a	w-a	w	w	w-a	w	w	w	w	Fluoride
A	A	a	A	a	a	A	a	a	a	w	w	w	w	Carbonate
a	a	a	a	a	a	a	a	a	a	w	w	w	w	Silicate
W	W <sub>21</sub>	g	W-I	A-I	W <sub>25</sub>	W	W-A <sub>33</sub>	W	W <sub>35</sub>	W <sub>37-38</sub>	W	W <sub>40</sub>	W-A <sub>43</sub>	Chloride
w	w	i	w-i	a-i	w	w	w-a	w	w	w	w	w	w-a	Brømide
W	w	i	W-A	A	W	A	W <sub>1</sub>	a	W	w	i	w	w-a	Iodide
a-i	I	I	a	a	A	W	a	a	W	w	i	i	i	Cyanide
i	I	w	i	w-a	A	w	a	w-a	w-a	w	w	w		Ferrocyanide
w	w	i	a	A	A	A <sub>20</sub>	a <sub>1</sub>	a	A	a <sub>30</sub>	a <sub>30</sub>	a <sub>41</sub>		Ferricyanide
A	a	g <sub>23</sub>	A	A	A <sub>20</sub>	w	W	W	W <sub>34</sub>	w	w	w		Thiocyanate
w	w	W	W	W	W <sub>26</sub>	w	w	w	w	w	w	w		Sulphide
w	w	w	w	w	w	w	w	w	w	w	w	w		Nitrate
w-a	W <sub>23</sub>	a	a	w-a	w-a	a	w	w	w-a	w	w	w		Chlorate
w	W	a	a	a	a	w-a	w	w	w	w	w	w		Tartrate
w	W	w-a	w-a	w-a	w-a	w-a	w	w	w	w	w	w		Citrate
w-a	a	a	a	a	a	w-a	w	w	w	w	w	w		Malate
w	a	w-a	a	w-a	w-a	w-a	w	w	w	w	w	w		Succinate
w	W	w	w-a	w-a	w <sub>25</sub>	w-a	W <sub>34</sub>	w	w	w	w	w		Benzoate
w	W	w	w-a	w-a	w	w	w	w	w	w	w	w		Salicylate
a	a	a	a	a	a	a	A	a	a		a	a	a	Acetate
a	a	a	a	a	a	a	a	a						Formate

10. Hydrogen sodium carbonate, W.
11. Tricalcium phosphate, A.
12. Ammonium magnesium phosphate, A.
13. Potassium aluminum sulphate, W.
14. Ammonium aluminum sulphate, W.
15. Potassium chromium sulphate, W.
16. Zinc sulphide, as a sphalerite, soluble in nitric acid with separation of sulphur; in hydrochloric acid only upon heating.
17. Manganese dioxide, easily soluble in hydrochloric acid; insoluble in nitric acid.

18. Nickel sulphide is rather easily decomposed by nitric acid; very difficultly by hydrochloric acid.
19. Cobalt sulphide, like nickel sulphide.
20. Ammonium ferrous sulphate, W.
21. Ammonium ferric chloride, W.
22. Potassium ferric tartrate, W.
23. Silver sulphide, only soluble in nitric acid.
24. Minium is converted by hydrochloric acid into lead chloride; by nitric acid into soluble lead nitrate and brown lead peroxide which is insoluble in nitric acid.
25. Tribasic lead acetate, W.
26. *Mercurius solubilis Hahnemannii*, A.
27. Basic mercuric sulphate, A.
28. Mercuric amido-chloride, A.
29. Mercuric sulphide, not soluble in hydrochloric acid, nor in nitric acid, but soluble in *aqua regia* upon heating.
30. Ammonium cupric sulphate, W.
31. Copper sulphide is decomposed with difficulty by hydrochloric acid, but easily by nitric acid.
32. Basic cupric acetate, partially soluble in water, and completely in acids.
33. Basic bismuth chloride, A.
34. Basic bismuth nitrate, A.
35. Sodium auric chloride, W.
36. Gold sulphide is not dissolved by hydrochloric acid, nor by nitric acid, but it is dissolved by hot *aqua regia*.
37. Potassium chlorplatinate, W-I.
38. Ammonium chlorplatinate, W-I.
39. Platinum sulphide is not attacked by hydrochloric acid, is but slightly attacked by boiling nitric acid (if it has been precipitated hot), but is dissolved by hot *aqua regia*.
40. Ammonium stannic chloride, W.
41. Stannous sulphide and stannic sulphide are decomposed and dissolved by hot hydrochloric acid, and are converted by nitric acid into oxide, which is insoluble in an excess of nitric acid. Sublimed stannic sulphide is dissolved only by hot *aqua regia*.

42. Antimonious oxide, soluble in hydrochloric acid, not in nitric acid.
43. Basic antimonious chloride, A.
44. Antimony sulphide is completely dissolved by hydrochloric acid, especially upon heating; it is decomposed by nitric acid, but dissolved only to a slight degree.
45. Calcium antimony sulphide, W-A.
46. Potassium antimony tartrate, W.
47. Hydrogen calcium malate, W.

## REAGENTS

With a few exceptions, all reagents should be of the highest purity obtainable and each sample lot tested before use. The fact that the bottle bears the label C. P. is no guarantee of its purity. It is especially important that the reagent be tested for the presence of the acid or basic radical it is employed to detect; e.g., "arsenic free zinc" should be tested for arsenic by the Gutzeit or Fleitmann test before being used. Sodium carbonate, employed in relatively large amounts for fusion purposes, should be of a high degree of purity, and should be tolerably free from foreign bases and acids.

## SOLUTIONS

### *Acids*

- *Conc. HCl*, sp. gr. 1.2, 39 % HCl by weight.
- *Dil. HCl*, 3 N, sp. gr. 1.05, 10 % HCl by weight.
- *Conc. HNO<sub>3</sub>*, sp. gr. 1.42, 70 % HNO<sub>3</sub> by weight.
- *Dil. HNO<sub>3</sub>*, 3 N, sp. gr. 1.10, 10 % HNO<sub>3</sub> by weight.
- *Conc. H<sub>2</sub>SO<sub>4</sub>*, sp. gr. 1.84, 98 % H<sub>2</sub>SO<sub>4</sub>.
- Dil. H<sub>2</sub>SO<sub>4</sub>*, 3 N, sp. gr. 1.09, 13 % H<sub>2</sub>SO<sub>4</sub>.
- Conc. HF*, 40 %.
- *Acetic Acid*, 5 N, sp. gr. 1.04, 30 % by weight. Dilute 285 cc. glacial acetic acid to a liter.

*Sulphurous Acid*, H<sub>2</sub>SO<sub>3</sub>, a solution saturated at 15° contains approximately 16.5 % H<sub>2</sub>SO<sub>3</sub>.

*Tartaric Acid*, 2 N, 150 g. in 1 liter.

*Aqua Regia*, 1 part of conc.  $\text{HNO}_3$  to 3 parts conc.  $\text{HCl}$ ; to be prepared only when needed.

$\text{H}_2\text{S}$  gas is prepared by the action of  $\text{HCl}$  (1:1) on  $\text{FeS}$ ; the gas should be washed by passing it through water before using.

### Bases

- *Conc. Ammonia*, sp. gr. 0.90, 28 %  $\text{NH}_3$ .
- *Dil. Ammonia*, sp. gr. 0.96, 10 %  $\text{NH}_3$ .
- *Sodium hydroxide*,  $\text{NaOH}$ , 4 N.

As the material used for qualitative purposes contains about 10 % of water, the amount needed for a 4 N solution will be  $4 \times 40 \times \frac{10}{9} = 177.7$  g. in 1 liter.

*Potassium hydroxide*,  $\text{KOH}$ , 4 N.

The grade used for analytical purposes contains about 20 % water; hence the quantity needed for a 4 N solution will be  $4 \times 56 \times \frac{4}{5} = 280$  g. in 1 liter.

- *Barium hydroxide*,  $\text{Ba}(\text{OH})_2$ , saturated solution.
- *Calcium hydroxide*,  $\text{Ca}(\text{OH})_2$ , saturated solution.

### Salts

- *Ammonium acetate*,  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ . 3 N. 250 g. in 1 liter.
- *Ammonium carbonate*,  $(\text{NH}_4)_2\text{CO}_3$   $\text{SO}_4$  free. Dissolve, without heating, 192 g. of the powdered salt in a mixture of 80 cc. of  $\text{NH}_4\text{OH}$  (sp. gr. 0.90) and 500 cc. of water. When solution is complete, dilute to 1 liter. The strength is approximately 4 N.
- *Ammonium chloride*,  $\text{NH}_4\text{Cl}$ , 4 N. 214 g. in 1 liter.
- *Ammonium molybdate solution*. To a mixture of 271 cc. of cold distilled water and 144 cc. of  $\text{NH}_4\text{OH}$  (sp. gr. 0.90), add 100 g.  $\text{MoO}_3$  and stir till solution is complete; slowly add this solution with constant stirring to a mixture of 489 cc.  $\text{HNO}_3$  (sp. gr. 1.42) and 1148 cc. of water. Allow the mixture to stand for 24 hours and then decant the clear liquid into a bottle.
- *Ammonium oxalate*,  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ . 35.54 g. in 1 liter.
- *Ammonium sulphide* (colorless),  $(\text{NH}_4)_2\text{S}$ . Saturate 3 parts of  $\text{NH}_4\text{OH}$  with  $\text{H}_2\text{S}$ , add 2 parts of ammonium hydroxide, and dilute with an equal volume of water.

- *Ammonium sulphide* (yellow),  $(\text{NH}_4)_2\text{S}$ . Digest the colorless undiluted  $(\text{NH}_4)_2\text{S}$  with flowers of sulphur in the proportion of 1 g. to the liter and then dilute with an equal volume of water.
- *Ammonium sulphate*,  $(\text{NH}_4)_2\text{SO}_4$ , N. 100 g. in 1 liter.
- *Barium chloride*,  $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$ , N. 122.17 g. in 1 liter. —
- *Bromine water*, saturated solution.
- *Calcium chloride*,  $\text{CaCl}_2$ , anhydrous, N. 55.6 g. in 1 liter.  
*Calcium sulphate*,  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ , saturated solution.  
*Chlorine water*, saturated solution.  
*Cobalt nitrate*,  $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ , for confirmatory tests for Al and Zn. 0.5 g. in 1 liter.
- *Copper sulphate*,  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ . 2 N. 249.6 g. in 1 liter.  
*Dimethylglyoxime*. Dissolve 5 g. in 500 cc. hot 95 % alcohol.
- *Ferric alum*,  $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24 \text{H}_2\text{O}$ , saturated solution.
- *Ferric chloride*,  $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ , \* 2 N. 180 g. in 1 liter.  
*Ferrous sulphate*,  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ . To be prepared in small amounts as needed.
- *Hydrochloroplatinic acid*,  $\text{H}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$ . 10 % solution.  
*Hydrogen dioxide*, 3 %.
- *Lead acetate*,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3 \text{H}_2\text{O}$ , † N. 189.5 g. in 1 liter.
- *Magnesia mixture*. Dissolve 110 g. of  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$  and 280 g. of  $\text{NH}_4\text{Cl}$  in a liter of distilled water; when solution is complete, add 261 cc. of ammonium hydroxide (sp. gr. 0.90), then add enough water to make the volume 2 liters.
- *Mercuric chloride*,  $\text{HgCl}_2$ . Saturated solution.
- *Phenolphthalein*, 1 % solution in 50 % ethyl alcohol.
- *Potassium acetate*,  $\text{KC}_2\text{H}_3\text{O}_2$ . Saturated solution.
- *Potassium chromate*,  $\text{K}_2\text{CrO}_4$ , N. 97.3 g. in 1 liter.
- *Potassium cyanide*,  $\text{KCN}$ , N. 65.2 g. in 1 liter.
- *Potassium dichromate*,  $\text{K}_2\text{Cr}_2\text{O}_7$ , N. 73.8 g. in 1 liter.
- *Potassium ferrocyanide*,  $\text{K}_4\text{Fe}(\text{CN})_6$ , N. 105.7 g. in 1 liter.
- *Potassium iodide*,  $\text{KI}, \frac{\text{N}}{2}$ . 83.1 g. in 1 liter.
- *Potassium nitrite*,  $\text{KNO}_2$ . 500 g. in 1 liter.
- *Potassium permanganate*,  $\text{KMnO}_4$ , N. 79.1 g. in 1 liter.

\* Should contain a little free HCl. † The solution should contain some free acetic acid.

— *Potassium thiocyanate*, KCNS, N. 97.2 g. in 1 liter.

— *Silver nitrate*, AgNO<sub>3</sub>,  $\frac{N}{4}$ . 42.5 g. in 1 liter.

*Silver sulphate*, Ag<sub>2</sub>SO<sub>4</sub>. Saturated solution.

*Sodium acetate*, NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, 4 N. 328 g. in 1 liter.

— *Sodium carbonate*, Na<sub>2</sub>CO<sub>3</sub> (dry). Saturated solution.

*Sodium cobaltic nitrite*, Na<sub>3</sub>Co(NO<sub>2</sub>)<sub>6</sub>. Dissolve 100 g. NaNO<sub>2</sub> in 300 cc. distilled water, slightly acidify with acetic acid, and then add 10 g. of Co(NO<sub>3</sub>)<sub>2</sub> · 6 H<sub>2</sub>O. Allow the solution to stand for 24 hours and filter if necessary. As the solution does not keep very well, only small amounts should be prepared at a time.

*Sodium nitroprusside*, Na<sub>2</sub>FeNO(CN)<sub>5</sub> · 2 H<sub>2</sub>O. 10% solution.

— *Sodium phosphate*, Na<sub>2</sub>HPO<sub>4</sub> · 12 H<sub>2</sub>O, N. 119 g. in 1 liter.

*Sodium stannite*, prepared as needed by adding to a little SnCl<sub>4</sub> solution sufficient NaOH solution to redissolve the precipitate which first forms.

— *Sodium thiosulphate*, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> · 5 H<sub>2</sub>O, N. 124 g. in 1 liter.

*Stannic chloride*, SnCl<sub>4</sub>,  $\frac{N}{2}$ . 32.7 g. in 1 liter.

— *Stannous chloride*,\* SnCl<sub>2</sub> · 2 H<sub>2</sub>O,  $\frac{N}{2}$ . 56.5 g. in 1 liter.

— *Stannous chloride* (for Bettendorff Test). Dissolve 113 g. of SnCl<sub>2</sub> · 2 H<sub>2</sub>O in 75 cc. of conc. HCl, and add a few pieces of C.P. tin foil and keep in a glass stoppered bottle.

*Starch paste*. Prepared as needed by mixing about 1 g. of powdered starch with a little cold water to form a thin paste and then adding it to 200 cc. of boiling water; boil for a minute, cool, and use. The solution does not keep, owing to the growth of molds. It may be kept for some time, however, if a preservative such as CS<sub>2</sub> is added.

\* The solution should be strongly acid with HCl; the addition of a little C.P. tin foil prevents the oxidation of the reagent.

## SOLVENTS

Alcohol, amyl, ( $C_6H_{11}OH$ ), C.P. Used in small amounts in the test for acetate.

Alcohol, ethyl, ( $C_2H_5OH$ ). 95 %, sp. gr. 0.815.

Benzol,  $C_6H_6$ , useful for dissolving sulphur.

Chloroform,  $CHCl_3$ , used for dissolving iodine.

Carbon disulphide,  $CS_2$ , used for dissolving iodine.

Ether, ethyl, ( $C_2H_5)_2O$ , solvent for fats and oils.

## DRY REAGENTS

Aluminum turnings, pure.

Ammonium chloride,  $NH_4Cl$ , C.P.

Ammonium nitrate,  $NH_4NO_3$ , C.P.

Borax,  $Na_2B_4O_7 \cdot 10 H_2O$ , C.P. and powdered.

Calcium carbonate,  $CaCO_3$ , alkali free.

Calcium fluoride,  $CaF_2$ ,  $SiO_2$  free.

Copper, strips.

Ferrous sulphate,  $FeSO_4 \cdot 7 H_2O$ , C.P.

Fusion mixture ( $Na_2CO_3 + K_2CO_3$ , dry and C.P.).

Iron filings.

Iron nails.

Lead dioxide,  $PbO_2$ , free from Mn.

Litmus paper, blue and red; to be kept in stoppered bottles.

Manganese dioxide,  $MnO_2$ , C.P. and powdered.

Microcosmic salt,  $NaNH_4HPO_4 \cdot 4 H_2O$ .

Paraffine, m.-p. 124°.

Potassium acid sulphate,  $KHSO_4$ , fused, C.P. in small lumps.

Potassium chlorate,  $KClO_3$ , C.P. powdered.

Potassium chloride,  $KCl$ , C.P.

Potassium cyanide,  $KCN$ , pure.

Potassium dichromate,  $K_2Cr_2O_7$ , C.P. powdered.

Potassium ferricyanide,  $K_3Fe(CN)_6$ , C.P.

Potassium nitrate,  $KNO_3$ , C.P. fine crystals.

Sand, sea.

- Silica,  $\text{SiO}_2$ , purified.  
Sodium acetate,  $\text{NaC}_2\text{H}_3\text{O}_2$ , C.P.  
Sodium acid carbonate,  $\text{NaHCO}_3$ , C.P.  
Sodium carbonate,  $\text{Na}_2\text{CO}_3$ , anhydrous, C.P. powdered.  
Sodium dioxide,  $\text{Na}_2\text{O}_2$ , C.P.  
Sodium sulphite,  $\text{Na}_2\text{SO}_3 \cdot 7 \text{ H}_2\text{O}$ , pure anhydrous.  
Starch, potato.  
Sulphur, flowers.  
Tin foil, C.P.  
Turmeric paper; to be kept in glass-stoppered bottles.  
Zinc, granulated, C.P.  
Zinc, granulated, arsenic-free.

## LIST OF APPARATUS

2 nests of beakers, Griffin, 1-4.	1 test tube cleaner.
1 graduated cylinder, 10 cc.	$\frac{1}{2}$ box gummed labels, # 217.
1 graduated cylinder, 50 cc.	1 doz. sheets filter paper, 18.5
1 wash bottle with fittings, 750 cc.	cm., S. & S. 595.
4 funnels, 6.5 cm.	1 pkg. filter paper, 12.5 cm., S. & S. 595.
1 funnel, 10 cm.	1 doz. fluted filters, 12.5 cm., S. & S. 588.
2 pieces cobalt glass.	1 test tube rack.
1 doz. test tubes (15 cm.)	1 test tube holder.
3 ft. glass rod.	1 filtering stand.
3 ft. glass tubing.	1 box matches, safety.
2 specimen bottles, 50 cc.	1 pair forceps (small).
2 watch glasses, 10 cm.	1 pipestem triangle.
2 watch glasses, 5 cm.	1 retort stand (2 rings).
1 watch glass, 12.5 cm.	2 bunsen burners, with hose.
1 florence flask, f. b. 50 cc.	1 blowpipe.
2 evaporating dishes, 10 cm.	1 stick charcoal.
2 evaporating dishes, 6.5 cm.	2 pieces wire gauze, 10 cm. square.
1 porcelain crucible.	1 triangular file.
1 horn spatula.	1 platinum wire.
1 rubber stopper, one hole, No. I.	1 platinum foil.
1 funnel cleaner.	1 towel.
1 sponge.	

## PREPARATION OF UNKNOWNS

In the making up of unknowns, stock solutions of the concentration 1 cc. = 100 mg. of metal are prepared. The quantity of salt necessary to dissolve in a liter to yield this strength is given in column 5 of the table below. By means of burettes or pipettes definite quantities of these standard solutions are measured out into student "unknown" bottles, homeopathic vials of 50 cc. capacity. For the analysis the student uses 25 cc. of his solution, the other half being reserved in case the analysis is to be repeated. The amounts of standard solutions pipetted out should be such as to yield a suitable concentration when the volume is diluted to 50 cc., *i.e.*, when the unknown bottle is filled. An example will make this clear. Pipette out into unknown bottle 1 cc. NaCl solution, 2 cc. Ca(NO<sub>3</sub>)<sub>2</sub>, and 1 cc. of NH<sub>4</sub>NO<sub>3</sub>, and then fill the bottle with distilled water. Since the student uses only 25 cc. of this solution, this quantity will contain 50 mg. Na, 100 mg. Ca, and 50 mg. NH<sub>4</sub>. Qualitative unknowns may be prepared of such a strength that the total weight of metal in 25 cc. never exceeds 1.5 grams, though it should usually be kept within 1 gram. The minimum will depend upon the scheme of analysis employed. It may be exceedingly small if the most sensitive tests are used, *e.g.*, the spectroscopic tests for the alkali and alkaline earth metals, the KCNS test for Fe, and the Marsh and Gutzeit tests for As and Sb. But if it is desired that the student report roughly the relative proportions of the ingredients present, precipitation methods will be largely used, which, by the size of the precipitates they yield, give indications of the approximate quantities of the metals present. In the latter case, the minimum quantity of metal present in 50 cc. will have to be much larger than it is in the first case.

TABLE EMPLOYED IN THE PREPARATION OF STANDARD STOCK SOLUTIONS \*

GROUP	SUBSTANCE	FORMULAR WEIGHT	SOLUBILITY OF SALT IN 100 PTS. OF COLD WATER	PER CENT. METAL	QUANTITY OF SALT TO BE DIS-SOLVED IN 1 LITER TO GIVE STRENGTH 1 CC. = 100 MG. OF METAL
I	AgNO <sub>3</sub> . . . .	170	v. s. <sup>1</sup> sol. in pres. of HNO <sub>3</sub>	63.5	157
	HgNO <sub>3</sub> .H <sub>2</sub> O . . .	280		71.5	140
	Pb(NO <sub>3</sub> ) <sub>2</sub> . . . .	331	48	62.5	160
	Pb(C <sub>2</sub> H <sub>8</sub> O <sub>2</sub> ) <sub>2</sub> .3H <sub>2</sub> O	379	46	54.6	183
II	Hg (NO <sub>3</sub> ) <sub>2</sub> .½(H <sub>2</sub> O)	333	sol. in pres. of HNO <sub>3</sub>	60	167
	HgCl <sub>2</sub> . . . .	271	7.4	74	135 <sup>2</sup>
	Bi(NO <sub>3</sub> ) <sub>3</sub> .5 H <sub>2</sub> O . .	484	sol. in pres. of HNO <sub>3</sub>	43	233
	Cu(NO <sub>3</sub> ) <sub>2</sub> .6 H <sub>2</sub> O . .	295	v. s.	21.5	465
	CuCl <sub>2</sub> .2 H <sub>2</sub> O. . .	170	120	37	270
	CuSO <sub>4</sub> .5 H <sub>2</sub> O . . .	249	40	25	400
	Cd(NO <sub>3</sub> ) <sub>2</sub> .4 H <sub>2</sub> O . .	308	v. s.	36	278
	CdCl <sub>2</sub> .2 H <sub>2</sub> O . . .	219	140	51	196
	3 CdSO <sub>4</sub> .8 H <sub>2</sub> O . . .	769	v. s.	43.5	230
	As <sub>2</sub> O <sub>3</sub> . . . .	198	4	75.5	( ) <sup>3</sup>
	Na <sub>2</sub> AsO <sub>3</sub> . . . .	170	v. s.	44	227
	Na <sub>2</sub> AsO <sub>4</sub> .12 H <sub>2</sub> O	402	28	18.7	( ) <sup>4</sup>
	As <sub>2</sub> O <sub>5</sub> . . . .	230	150	65	153
	SbCl <sub>3</sub> . . . .	226	sol. in pres. of HCl	53	188
	SnCl <sub>2</sub> .2 H <sub>2</sub> O . . .	225	v. s.	53	189
	SnCl <sub>4</sub> .5 H <sub>2</sub> O . . .	350	v. s.	34	294
	SnCl <sub>4</sub> . . . .	260	v. s.	46	218

<sup>1</sup> Very soluble.<sup>2</sup> This amount readily dissolves in 1 liter of water containing 50 g. of NaCl.<sup>3</sup> 33 g. in 1 liter HCl (1 : 1) gives strength 1 cc. = 25 mgs. As.<sup>4</sup> 267 g. in 1 liter will give strength 1 cc. = 50 mgs. As.

\* Taken from an article published in *School Sci. and Math.*, Vol. X., No. 6, by one of us (L. J. C.).

TABLE EMPLOYED IN THE PREPARATION OF STANDARD STOCK SOLUTIONS — *Continued*

GROUP	SUBSTANCE	FORMULAR WEIGHT	SOLUBILITY OF SALT IN 100 PTS. OF COLD WATER	PER CENT. METAL	QUANTITY OF SALT TO BE DIS- SOLVED IN 1 LITER TO GIVE STRENGTH 1 CC. = 100 MG. OF METAL
III	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ .	666	107	8.1	( ) <sup>1</sup>
	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ . . .	242	74	11.1	( ) <sup>2</sup>
	$\text{Al}(\text{NO}_3)_3 \cdot 8\text{H}_2\text{O}$ .	261	v. s.	10.3	970
	$\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ .	716	v. s.	14.6	690
	$\text{K}_2\text{Cr}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$	1000	20	5.2	( ) <sup>3</sup>
	$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ .	400	v. s.	13	770
	$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ . . .	266.5	v. s.	19.6	510
	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . . .	278	60	20	500
	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ .	404	v. s.	14	715
	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . . .	270	v. s.	20.7	482
	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .	291	50	20	500
	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ . . .	238	v. s.	25	400
	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ . . .	280	106	21	475
	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .	291	v. s.	20	500
	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . . .	238	v. s.	24.5	407
	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ . . .	281	50	21	475
	$\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ . . .	223	123	25	400
	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ . . .	198	150	28	360
	$\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .	287	v. s.	19	527
	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ . . .	288	135	22.5	445
	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .	298	v. s.	22	455
	$\text{ZnCl}_2$ . . . . .	136	v. s.	48	208

<sup>1</sup> 620 g. in 1 liter will give strength 1 cc. = 50 mg. Al.<sup>2</sup> 450 g. in 1 liter will give strength 1 cc. = 50 mg. Al.<sup>3</sup> 192 g. in 1 liter will give strength 1 cc. = 10 mg. of Cr.

TABLE EMPLOYED IN THE PREPARATION OF STANDARD STOCK SOLUTIONS — *Continued*

GROUP	SUBSTANCE	FORMULAR WEIGHT	SOLUBILITY OF SALT IN 100 PTS. OF COLD WATER	PER CENT. METAL	QUANTITY OF SALT TO BE DIS- SOLVED IN 1 LITER TO GIVE STRENGTH 1 CC.— 100 MG. OF METAL
IV	BaCl <sub>2</sub> ·2 H <sub>2</sub> O . . .	244	41	56	179
	Ba(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·H <sub>2</sub> O .	273	63	50	200
	Sr(NO <sub>3</sub> ) <sub>2</sub> ·4 H <sub>2</sub> O .	284	40	31	324
	Sr(NO <sub>3</sub> ) <sub>2</sub> . . .	212	39	41.3	242
	SrCl <sub>2</sub> ·6 H <sub>2</sub> O . . .	266	106	33	304
	CaCl <sub>2</sub> . . . .	111	v. s.	36	278
	Ca(NO <sub>3</sub> ) <sub>2</sub> ·4 H <sub>2</sub> O .	236	v. s.	17	590
V	MgSO <sub>4</sub> ·7 H <sub>2</sub> O . . .	246	77	9.7	( ) <sup>1</sup>
	Mg(NO <sub>3</sub> ) <sub>2</sub> ·6 H <sub>2</sub> O .	256.5	200	9.4	1060
	MgCl <sub>2</sub> ·6 H <sub>2</sub> O . . .	203.5	365	11.9	837
	NaCl . . . .	58	35	40	250
	Na <sub>2</sub> HPO <sub>4</sub> ·12 H <sub>2</sub> O .	358	9.3	13	( ) <sup>2</sup>
	NaNO <sub>3</sub> . . . .	85	80	27	371
	KCl . . . .	75	32	52	192
	KHSO <sub>4</sub> . . . .	136	v. s.	28.5	350
	KNO <sub>3</sub> . . . .	101	31	39	257
	NH <sub>4</sub> Cl . . . .	53	33	34	294
	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> . . . .	132	76	27.5	365
	NH <sub>4</sub> NO <sub>3</sub> . . . .	80	200	22.5	445
	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> . . .	132	36.5	27.5	365
	LiCl . . . .	42	80	16.7	600
	LiNO <sub>3</sub> . . . .	69	48	10	( ) <sup>3</sup>

<sup>1</sup> 515 g. in 1 liter will give strength 1 cc.=50 mg. Mg.<sup>2</sup> 77 g. in 1 liter will give strength 1 cc.=10 mg. Na.<sup>3</sup> 500 g. in 1 liter will give strength 1 cc.=50 mg. Li.



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